

INSTITUTE OF METALS DIVISION

1946

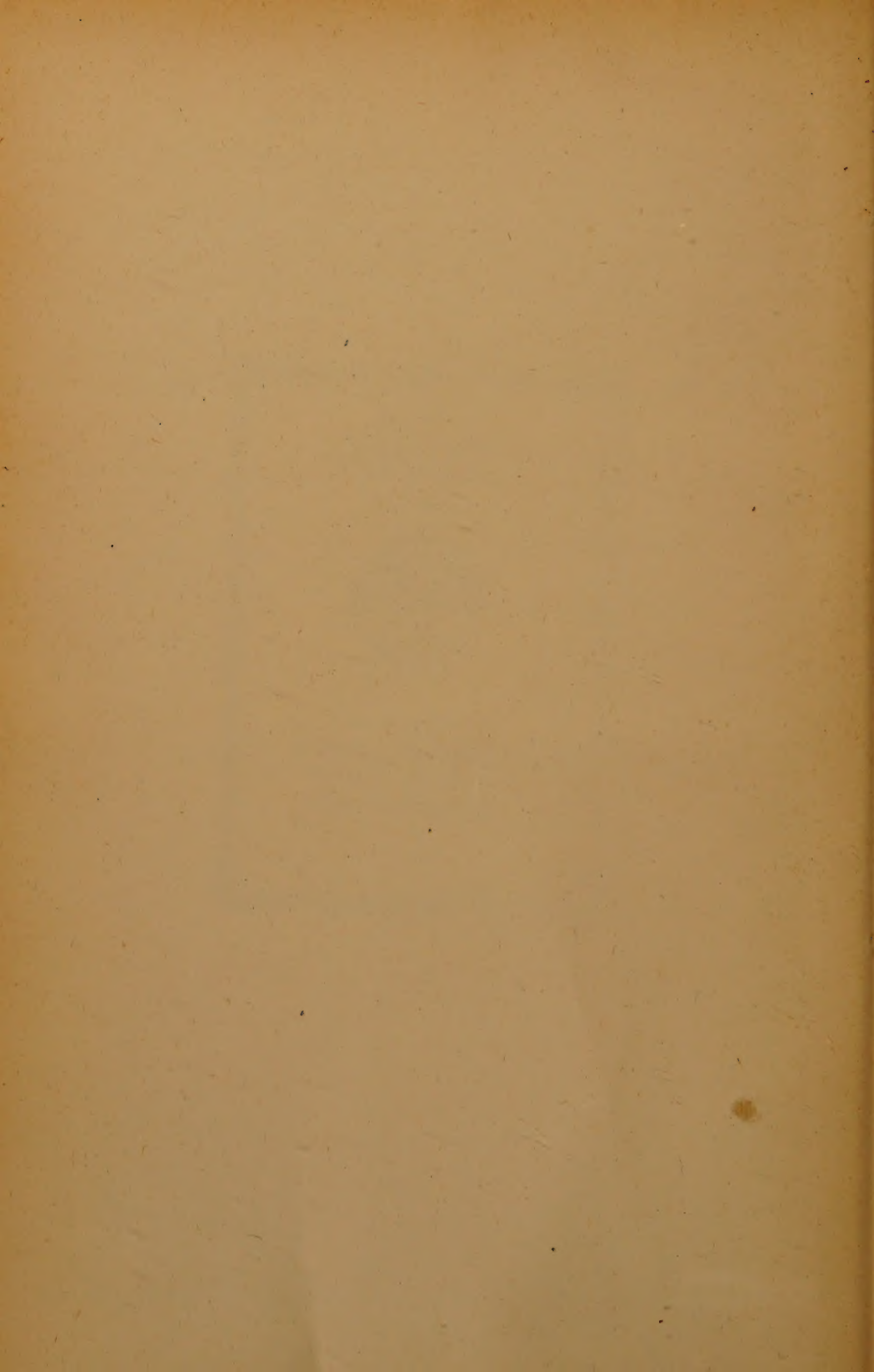
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TRANSACTIONS

OF THE

AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS

(INCORPORATED)

and Petroleum

Volume 166

INSTITUTE OF METALS DIVISION

1946

TECHNICAL PAPERS AND DISCUSSIONS AND SYMPOSIA PRESENTED BEFORE THE

DIVISION AT MEETINGS HELD AT NEW YORK, OCTOBER 16-17, 1945,

AND AT CHICAGO, FEBRUARY 25-28, 1946.

PUBLISHED BY THE INSTITUTE
AT THE OFFICE OF THE SECRETARY

29 WEST 39TH STREET
NEW YORK 18, N.Y.

Notice

This volume is the twentieth of a series constituting the official proceedings of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers. It deals with nonferrous metals and includes papers presented at the New York Meeting, Oct. 16-17, 1945, and the Chicago Meeting, Feb. 25-28, 1946. The complete list of publications and proceedings, including the present volume, is as follows:

- 1908-1911 *Transactions* of the American Brass Founders' Association: 1908, Vols. 1 and 2; 1909, Vol. 3; 1910, Vol. 4; 1911, Vol. 5.
- 1912-1916 *Transactions* of the American Institute of Metals, Vols. 6-10.
- 1917-1918 *Journal* of the American Institute of Metals, Vols. 11-12.
- 1919-1926 *TRANSACTIONS* of the American Institute of Mining and Metallurgical Engineers, Volumes 60, 64, 67, 68, 69, 70, 71 and 73.
- 1927-1928 *PROCEEDINGS* of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers, two volumes, of which the later is now designated Vol. 78 of the A.I.M.E. *TRANSACTIONS*.
- 1929-1946 *TRANSACTIONS* of the American Institute of Mining and Metallurgical Engineers, Volumes 83, 89, 93, 99, 104, 111, 117, 122, 124, 128, 133, 137, 143, 147, 152, 156, 161, and 166, Institute of Metals Division.

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PRINTED IN THE UNITED STATES OF AMERICA

THE MAPLE PRESS COMPANY, YORK, PA.

FOREWORD

HERE again, in Volume 166 of the TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, which is the twentieth volume of the proceedings of what is now known as the Institute of Metals Division, is the annual evidence of a remarkable cooperative effort.

Included are some thirty-five contributions from industrial, academic, and governmental investigational institutions. The total man-hours that went into the work leading to these publications is practically impossible of estimation. To be sure, it may be assumed that full value was received for the cost of the direct investigational work, but there remained no obligation whatsoever to make the material available for general benefit. Also, it is probably not generally recognized how much extra work is involved in preparing such papers for publication. It is almost invariably the rule that the authors find it necessary to do a considerable amount of the writing and arrangement on their own time. After the authors have nursed their brain child into some fairly respectable form it is usual that it be subjected to criticism by their immediate superiors and colleagues. From there, the prospective paper then goes to the organization's editorial committee, where usually it is given another inspection by an additional two or three individuals. All of this takes man-hours, many of them "extracurricular." Finally, the paper is then ready for submission to some technical, scientific, or professional society for presentation and possible publication.

If the paper is submitted to the Institute of Metals Division it goes to the Publications Committee, under the chairmanship of E. A. Anderson this year. The members of this committee or qualified readers to whom they may refer it for expert opinion examine the paper with respect to its suitability for presentation at some meeting of the Division in view of the membership's general interest. This committee has the very disagreeable job of looking gift horses in their mouths and declining any that appear unsuitable from the standpoint of interest to the members and quality of the paper.

After having been critically examined, and perhaps revised according to suggestions of readers, the paper may be accepted for publication. Then, the Programs Committee, under A. A. Smith, Jr., this year, must arrange for its presentation at some meeting of the Division or Institute, seeing that the paper is accompanied by others on related subjects and that opportunity is provided for free discussion. Incidentally, the Programs Committee often—for example, in the case of the symposium on extrusion published in this volume—takes the initiative, and by direct solicitation obtains papers on specific subjects for definite meetings. Before presentation, the paper must be preprinted, and distributed either before or at the meeting, which mechanical functions are performed so ably by the central office of the Institute as to be generally overlooked. After presentation, the discussion of the paper must be arranged and printed and, finally, all the papers assembled to make up a volume such as this.

There is represented in this volume another instance of cooperative work in the symposium on powder metallurgy, which was arranged by the Powder Metallurgy Committee under F. N. Rhines as chairman. Some twenty individuals serve on such a committee as this, giving unstintedly of their time, and the results of those efforts are particularly evident in the instance of the Powder Metallurgy Committee by reason of the manner in which an exceedingly confused and controversial subject was brought into a state of excellent organization in a matter of a very few years.

This volume, then, is the culmination of all these activities. It is evident that the amount of labor involved, most of which is contributed gratuitously, is enormous. It may well be asked: What is the reason so many individuals do a great deal of work over and beyond that necessary for the maintenance of their jobs and livelihoods? I will not attempt to answer the question but will merely suggest that our many technical, scientific, and professional societies are excellent examples of the fact that cooperative effort toward common good can be successful. Is there any fundamental reason why such cooperative effort toward even more important common goals cannot be expanded to embrace all the peoples of the world?

L. W. KEMPF, *Chairman,*
Institute of Metals Division.

CLEVELAND, OHIO

June 12, 1946.

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ANNUAL AWARD CERTIFICATE OF THE INSTITUTE OF METALS DIVISION

In 1933, the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers established its annual award of an engraved certificate to the author or authors of the paper that in the opinion of the award committee represents the most notable contribution to metallurgical science among the papers that have been accepted by the Division for presentation at one of its meetings and have been published by the Institute within the three years preceding the date of award. The award is made by the Division each February. There are no restrictions with respect to nationality, age or occupation of the author or authors.

Awards have been made as follows:

- 1934 Robert F. Mehl and Charles S. Barrett: Studies upon the Widmanstätten Structure, I—Introduction. The Aluminum-silver System and the Copper-silicon System. *TRANSACTIONS* (1931) **93**, 78-110.
- 1935 R. A. Anderson, M. L. Fuller, R. L. Wilcox and J. L. Rodda: The High-zinc Region of the Copper-zinc Phase Equilibrium Diagram. *TRANSACTIONS* (1934) **111**, 264-292.
- 1936 Cyril S. Smith and W. Earl Lindlie: A Micrographic Study of the Decomposition of the Beta Phase in the Copper-aluminum System. *TRANSACTIONS* (1933) **104**, 69-105.
- 1937 Arthur Phillips and R. M. Brick: Effect of Quenching Strains on Lattice Parameter and Hardness Values of High-purity Aluminum-copper Alloys. *TRANSACTIONS* (1934) **111**, 94-112.
- 1938 William L. Fink and Dana W. Smith: Age-hardening of Aluminum Alloys, I—Aluminum-copper Alloy. *TRANSACTIONS* (1936) **122**, 284-293.
- 1939 Frederick N. Rhines and Robert F. Mehl: Rates of Diffusion in the Alpha Solid Solutions of Copper. *TRANSACTIONS* (1938) **128**, 185-221.
- 1940 Alden B. Greninger: Martensite Transformation in Beta Copper-aluminum Alloys. *TRANSACTIONS* (1939) **133**, 204-221.
- 1941 S. E. Maddigan and A. I. Blank: Recovery and Recrystallization in Long-time Annealing of 70-30 Brass. *TRANSACTIONS* (1940) **137**, 170-190.
- 1942 F. N. Rhines: A Metallographic Study of Internal Oxidation in the Alpha Solid Solutions of Copper. *TRANSACTIONS* (1940) **137**, 246-288.
- 1943 J. D. Hanawalt, C. E. Nelson and J. A. Peloubet: Corrosion Studies of Magnesium and Its Alloys. *TRANSACTIONS* (1942) **147**, 273-298.
- 1944 A. H. Geisler, C. S. Barrett and R. F. Mehl: Aging in the Solid Solution of Silver in Aluminum. *TRANSACTIONS* (1943) **152**, 182-200.
- 1945 William M. Baldwin, Jr.: Effect of Rolling and Annealing upon the Crystallography, Metallography, and Physical Properties of Copper Strip. This volume, page 591.
- 1946 P. W. Bakarian and C. H. Mathewson: Slip and Twinning in Magnesium Single Crystals at Elevated Temperatures. *TRANSACTIONS* (1943) **152**, 226-254.

THE INSTITUTE OF METALS LECTURE

An annual lectureship was established in 1921 by the Institute of Metals Division, which has come to be one of the important functions of the Annual Meeting of the Institute. In 1934 the Division established the custom of presenting a certificate to each lecturer.

A number of distinguished men from this country and abroad have served in this lectureship. The roll is quoted below:

- 1922 Colloid Chemistry and Metallurgy. By Wilder D. Bancroft.
- 1923 Solid Solution. By Walter Rosenhain.
- 1924 The Trend in the Science of Metals. By Zay Jeffries.
- 1925 Action of Hot Wall: a Factor of Fundamental Influence on the Rapid Corrosion of Water Tubes and Related to the Segregation in Hot Metals. By Carl Benedicks.
- 1926 The Relation between Metallurgy and Atomic Structure. By Paul D. Foote.
- 1927 Growth of Metallic Crystals. By Cecil H. Desch.
- 1928 Twinning in Metals. By C. H. Mathewson.
- 1929 The Passivity of Metals, and Its Relation to Problems of Corrosion. By Ulick R. Evans.
- 1930 Hard Metal Carbides and Cemented Tungsten Carbide. By S. L. Hoyt.
- 1931 X-ray Determination of Alloy Equilibrium Diagrams. By Arne Westgren.
- 1932 The Age-hardening of Metals. By Paul D. Merica.
- 1933 Present-day Problems in Theoretical Metallurgy. By Georg Masing.
- 1934 Ferromagnetism in Metallic Crystals. By L. W. McKeehan.
- 1935 Gases in Metals. By C. A. Edwards.
- 1936 Diffusion in Solid Metals. By Robert F. Mehl.
- 1937 Refractories. By R. S. Hutton.
- 1938 The Nature of Metals as Shown by Their Properties under Pressure. By P. W. Bridgman.
- 1939 The Creep of Metals. By D. Hanson.
- 1940 Acceleration of Rate of Corrosion by High Constant Stresses. By Edgar H. Dix, Jr.
- 1941 Some Fundamentals of the Flow and Rupture of Metals. By George Sachs.
- 1942 Notes on the History, Manufacture, and Properties of Wrought Brass. By Wm. Reuben Webster.
- 1943 Applications of the Electron Microscope in Metallurgy. By V. K. Zworykin.
- 1944 Some Problems in Organizing Industrial Research. By W. M. Peirce.
- 1945 A New Microscopy and Its Potentialities. By Charles S. Barrett.

TECHNICAL PAPERS
AND
DISCUSSIONS

Electron Metallographic Methods and Some Results for Magnesium Alloys

By R. D. HEIDENREICH,* C. H. GEROULD,* AND R. E. McNULTY*

(Chicago Meeting, February 1946)

THE electron microscope techniques and their application to magnesium alloys that are to be discussed in this paper are the result of research at The Dow Chemical Co. over the past three years. The viewpoint underlying the work is not wholly metallurgical, but has evolved through a variety of problems related to the physics and chemistry of surfaces. It can be said that the interest and stimulus were closely associated with a desire to employ effectively the electron microscope in research concerning the properties of solids as related to their physical structure. Only a portion of this work will be described here, and, consequently, many points of interest and debate are of necessity either only briefly recognized or are completely omitted.

As has been pointed out by Desch,¹ a great deal of the knowledge of the structure of metals has been obtained through microscopic studies of the surfaces of metallic specimens prepared in a particular manner. This information, when added to that obtained by means of thermal, electrical, X-ray, dilatometric and other methods, has been of great value both from a theoretical and a practical viewpoint. With the introduction of new instruments such as the electron diffraction camera and the electron microscope, it would be expected that still more informa-

tion could be obtained. These two instruments have in many instances been very effective when directed toward the investigation of metallic surfaces, provided the proper methods of surface preparation were employed. Experience shows that the problems of surface preparation greatly limit the general application of these instruments to metallographic studies.

It was found necessary to discard the standard metallographic procedures in applying the electron microscope to magnesium alloys and to work out new methods, which were required to satisfy certain conditions. These methods are unique to magnesium only in the specific chemical reactions occurring during etching.

The presentation of the methods and results will be ordered as follows:

1. Electron Microscopy of Surfaces.
2. Surface Preparation of Magnesium Alloys.
3. Discussion of Microstructures.
 - a. Pure Magnesium and Single-crystal Studies.
 - b. Types of Precipitation.
 - c. Some Common Structures.
 - d. Special Micrographs and Techniques.
 - e. Structure of Mg-Al Solid Solutions.
4. Correlation of "Fine Structure" with Corrosion Behavior of Magnesium Alloys.

ELECTRON MICROSCOPY OF SURFACES

It seems unnecessary to present more than a very brief recapitulation of the features of the present-day electron micro-

* Manuscript received at the office of the Institute Nov. 13, 1945. Issued as T.P. 1979 in METALS TECHNOLOGY, April 1946.

* The Dow Chemical Co., Midland, Michigan.

¹ References are at the end of the paper.

scope and the problem of applying it to solid surfaces. Numerous articles and papers deal with the design, construction and principles of this instrument.* Its

work. Fig. 1 illustrates the principle of such a replica, while the actual steps² required to produce the final film are enumerated below:



FIG. 1.—REPRODUCTION OF SURFACE CONTOURS BY THE POLYSTYRENE-SILICA REPLICA.

specific application to surface-contour investigations has been described²⁻⁵ in detail.

The use of an electron beam as illuminating radiation imposes severe restrictions on the type of specimen that may be examined. Among the restrictions are:

1. The most satisfactory images are obtained with transmission specimens. The penetrating power of a stream of electrons is small, and 60-kv. electrons do not produce images of high quality after penetrating more than about 300\AA of matter.

2. It is necessary that the specimen be in an evacuated space (about 10^{-4} mm. Hg), since the presence of air or other gases causes ionization.

Point 1 is the major consideration in metallographic applications. If the surfaces of matter in bulk are to be examined with a transmission-type electron microscope, it is necessary that not more than about 300\AA . be penetrated in forming the image. The present solution to this difficulty is the use of a surface replica, or thin film of material that has impressed into it all of the contours of the original surface. Of the several suggested methods^{2,4} of producing such replica films, only the polystyrene-silica replica will be considered for this

1. Onto the prepared surface is pressure-molded a thermoplastic, polystyrene, which produces a first impression of the surface contours.

2. The polystyrene molding is separated from the original surface mechanically or, if necessary, by dissolution of the sample in an appropriate reagent.

3. Silica is vaporized onto the surface of the polystyrene molding to produce the final replica film.

4. The silica film, still on the molding, is scribed into $\frac{1}{8}$ -in. squares and the whole is then placed in a dish containing a solvent consisting of ethyl bromide with 10 per cent benzene. The silica squares are released from the polystyrene within a few minutes and are thereupon transferred to fresh solvent for rinsing. They are then picked up from the rinse solution on $\frac{1}{8}$ -in. disks of 200-mesh stainless steel, which serve as specimen supports for the electron microscope. The portions of the film stretched over the holes in the screen are imaged by the electron microscope and photographed directly. The intensity variations in the final image result from thickness variations in the replica film, which in turn depend on the contours of the original surface as illustrated in Fig. 1.

Although such a process may appear complicated and clumsy, a replica may be turned out in less than 45 min. when the

* For discussion and references see A. F. Prebus: *Alexander's Colloid Chemistry*, 5, 152. Reinhold Pub. Co. New York (1945).

equipment and technique have been organized. In general, more time is spent examining the fields in the microscope than in making the replica. Many hundreds of surfaces have been examined in these laboratories by this method.

The faithfulness of reproduction of surface contours has been investigated,² with the following results:

1. The electron images of the silica replica are very similar in general appearance to ordinary micrographs of the original surface (see ref. 3).

2. Structural details or contour changes of less than 100\AA (ref. 2) in size can be detected using the silica replica. Although the resolution of the magnetic electron microscope is estimated to be about one third of this figure, the resolution obtainable with the replica is still some 30 times better than that of the light metallographic microscope. The depth of focus of the electron microscope is of the order of 10 times that of the light microscope, which means that quite large elevation changes can be accommodated.

All of the electron micrographs of this paper were made as just described, using an RCA electron microscope, type B.

Electron micrographs of the surface contours of a specimen are only a part of the information desired. Such images give no more information than can be deduced from size and shape. With properly prepared surfaces, however, further information as to the crystallographic features of the surface can be obtained by means of electron diffraction.^{6,7} By the so-called reflection method, the identity of the surface projections normal to the incident beam, and sufficiently thin to allow transmission, can often be ascertained; that is, the slow-etching phases in a metal specimen will produce the greater portion of the diffraction pattern. This matter is discussed in ref. 7 and several applications will be found there.

SURFACE PREPARATION OF MAGNESIUM ALLOYS

The method used at present for preparing magnesium specimens for both electron microscope examination and electron diffraction identification of phases has been found to be uniquely successful. No effort will be made to trace the extensive development, which was initiated when standard etchants for light microscope work were found quite inadequate (see p. 29) for electron microscopy. Rather, the conditions and method are first outlined and then compared with standard metallographic results.

The requirements for a metallographic surface preparation suitable for electron microscope and electron diffraction work are considered to be the following:

1. Sufficient metal must be removed from the ground surface by chemical methods to ensure the absence of any distorted or fragmented metal in the regions to be studied.

2. The etching reagent must be selective for the structures in question; i.e., the rates of dissolution of different phases or components must differ sufficiently to produce the required surface contours. The order of attack of the various phases present should be known.

3. The etching reagent should not produce surface films or stains that cannot be removed by subsequent rinsing.

4. The chemical behavior during etching must be controlled so that no component of the alloy is dissolved and then redeposited on the etched surface (see ref. 7).

5. The rinsing procedure employed in conjunction with the etchant must remove any reaction products deposited and produce a surface that is free of oxide or hydroxide films and grease. The criterion for cleanliness is simply that electron diffraction reflection from the surface shall yield a pattern for the metallic constituents.

This set of requirements is not restricted to magnesium alloys, but applies to any

alloy system. The first requirement for most alloys is usually met by electrolytic polishing methods. Requirements 2, 3 and 4 are specific to the alloy being investigated. Requirement 5 has been satisfied for several alloy systems by a series of rinses described in ref. 7. These rinses were first employed for magnesium surfaces.

For nearly all magnesium alloys, requirements 1, 2, 3 and 4 are satisfied by a single chemical reagent, which removes sufficient metal in a short time to eliminate the damage done by grinding and also produces a selective etch attack. This reagent is an anhydrous, organic etchant consisting of a mixture of one part methyl iodide and one part dry methyl alcohol to which is added a crystal or two of iodine to initiate the reaction.

The actual procedure employing the methyl iodide reagent and the subsequent rinses is as follows:

1. The specimen is abraded on No. 1 metallographic paper under dry benzene.

2. It is immediately transferred to the etchant, which is generally used in 25-c.c. amounts for samples roughly $\frac{1}{2}$ in. square. A small glass vessel about 5 cm. in diameter and 10 cm. deep is convenient. The mixture usually is heated slightly in warm water to aid in starting the reaction. The etchant is mixed as used.

3. After the reaction has continued vigorously for 2 to 3 min., the specimen is rapidly transferred to the first of a series of three rinse solutions. The purpose of this sequence of rinses is to displace the etching solution with an inert liquid without deposition of foreign materials. The samples are agitated for about 5 sec. in each and transferred rapidly to the next.

Rinse 1 consists of 1 part methanol: 1 part acetone + 0.5 per cent formic acid.

Rinse 2 is the same as rinse 1 but without formic acid.

Rinse 3 is clean, dry benzene.

4. Dry in a blast of clean, warm air.

The 25 c.c. of etchant and 50-c.c. batches of each rinse may be employed for several samples before it is necessary to mix a new set.

The chemistry involved in the etching reaction has not been investigated. Methoxy magnesium iodide is a possible product, although probably it is unstable. The reaction is very vigorous when once started and may heat the etchant sufficiently to boil away the methyl iodide. Fortunately, the rate is quite sensitive to temperature and hence can be easily controlled by heating or cooling in a stream of water.

Caution must be exercised in using the etchant. The hands should be kept away from the top of the vessel during etching, by the use of long-handled Monel-metal tweezers with which to hold the sample. The specimen must be held under the surface of the etchant, because of the copious gas evolution. Both the reagent and the fumes given off will produce blisters on the hands, followed by drying and painful cracking. Gloves of any kind are not recommended. The tweezers and frequent washing of the hands are the safest means for preventing burns.

Numerous organic halides have been tried, but methyl iodide is generally the most satisfactory. Alcohols higher than methyl greatly reduce the rate of attack.* In general, the rate decreases as the amount of hydrocarbon, either as alcohol or halide, increases. The rate of attack also decreases in the order iodide, bromide, and chloride.

The initiation of the etching reaction deserves some discussion, since some early difficulties were experienced here. It was found that for pure magnesium the reaction could be converted from an isolated pit attack to a general surface reaction only when the specimen was prepared in a certain way. The presence of films of hydroxide or oxide on the surface is sufficient to allow

* Ethanol is recommended for electron diffraction studies on magnesium-zinc alloys.

only a few isolated spots to undergo reaction with the etchant.

Immediately after grinding, a magnesium specimen abraded in air will yield an elec-

methyl iodide reagent than does the bulk metal.

As mentioned, a crystal or so of iodine is employed in the reagent. It does not

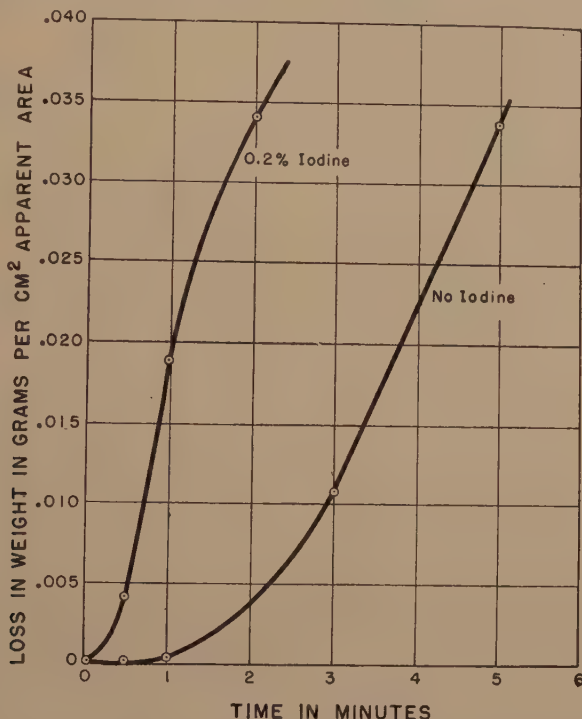


FIG. 2.—LOSS IN WEIGHT OF PURE MAGNESIUM IN METHYL IODIDE ETCHANT AT 75° TO 85°F.

tron diffraction pattern for magnesium oxide. Contact with liquid water will result in the formation of magnesium hydroxide. Grinding under a medium such as dry, distilled benzene greatly reduces the tendency to form oxides or hydroxides.

The state of the surface, although free of films, greatly influences the starting of the reaction. A pure magnesium surface formed by actual polishing on broadcloth under benzene will not be uniformly attacked, but again will be pitted severely. This is attributed to the formation of a polish layer (ref. 6, chap. 13) which has been shown to possess considerably different physical and chemical properties from the bulk material. This layer on magnesium appears much less reactive with the

seem to affect the general nature of the etch attack, but does greatly aid in sensitizing the reaction. The sensitizing by iodine is demonstrated for pure magnesium by the curves of Fig. 2, where weight loss per unit apparent area is plotted against time. With no iodine present, the surface is badly pitted after one minute in the reagent and the attack does not become general until 3 to 4 min. have elapsed. With iodine present, however, the reaction first starts at a few scattered spots on the surface and then rapidly spreads until the entire surface takes part.

With magnesium-aluminum solid solutions, it was found to be nearly impossible to start the reaction without iodine present. The attack of the various com-

ponents in a magnesium-aluminum alloy are, in the order of decreasing rate: (1) pure magnesium, (2) Mg-Al solid solution, (3) intermetallic compound $Mg_{17}Al_{12}$. The solid solutions and intermetallic compounds are generally more slowly attacked, except the magnesium-cadmium system, in which the rate is in excess of that for pure magnesium. None of the metals, zinc, aluminum, cadmium, beryllium, are themselves reactive, although their solid solutions in magnesium are attacked.

Etchants other than methyl iodide can be employed and clean surfaces obtained if the rinsing schedule is maintained. The type of attack is not so desirable, however, and the methyl iodide reagent is far more sensitive to structural heterogeneities, as will be seen in the following pages.

The chief disadvantage of the methyl iodide reagent is the macroroughness of the finished surfaces. They are generally quite rolling or wavy, as a result of the gas evolution during etching, and consequently are not satisfactory for light microscopy. The depth of the etch is generally greater than that recommended for high-magnification light microscopy. For electron microscopy and electron diffraction, however, such surfaces are quite suitable. This, again, is a matter of the focal depth of the two types of microscopes.

To illustrate more clearly the character of the etchant used, two light micrographs, two electron micrographs and two electron diffraction patterns are given comparing the conventional acetic glycol etch with the methyl iodide etch. Fig. 3a is a light micrograph of a Mg + 8 per cent Al alloy in the heat-treated and aged condition. The etchant is the acetic glycol used generally on magnesium.⁸ A very fine pearlitic type of precipitation is evident, with apparently some background within the grains, the details of which are not resolvable. There is a line structure within some of the grains, as though possibly the result of grain refinement, but the true significance of these

lines is not evident. Fig. 3c is an electron micrograph of the same specimen with the same etch as in Fig. 3a. The pearlitic type of precipitation is seen to be coarse platelets. There is a structure within the grain consisting of a very fine distribution of platelets with a line of coarser platelets through the center of the grain. This is evidently one of the intragranular lines seen in Fig. 3a.

Fig. 3b is a light micrograph of the same specimen, prepared with the methyl iodide etchant. Note the extreme waviness of the surface and the inability of the light microscope to maintain focus throughout the field. Fig. 3d is of the same surface as Fig. 3b viewed with the electron microscope. The greater depth of focus of the latter instrument is clearly apparent. The same general features are present in both Figs. 3c and 3d, but a greater sharpness and clarity of outline is seen in Fig. 3d. More fine detail is also present. Fig. 3e is an electron diffraction pattern from the surface of Fig. 3a showing a pattern for $Mg(OH)_2$, while Fig. 3f is from the surface of Fig. 3b, showing the pattern of $Mg_{17}Al_{12}$. Thus, with the conventional metallographic techniques, a surface film is formed, which obscures the details. An etchant such as the methyl iodide, by contrast, leaves no film and the true metallic details can be seen in sharp outline.

DISCUSSION OF MICROSTRUCTURES

No one field of magnesium metallurgy will be covered in detail, but rather a short survey will be given, illustrative of the accomplishments of the electron microscope as used in these laboratories.

Pure Magnesium and Single-crystal Studies

The high resolution of the electron microscope can be used to good advantage in studies of small amounts of impurities in pure metal and in research in crystal mechanics. Such things as slip-line spacing,



FIG. 3.—ALLOY OF MAGNESIUM PLUS 8 PER CENT ALUMINUM IN THE HEAT-TREATED AND AGED CONDITION.

Acetic Glycol Etchant

- a. Light micrograph. Original magnification 250.
 c. Electron micrograph. Original magnification 5000.
 e. Electron diffraction reflection pattern for a magnesium hydroxide.

Methyl Iodide Etchant

- b. Light micrograph. Original magnification 250.
 d. Electron micrograph. Original magnification 5000.
 f. Electron diffraction reflection pattern for $\text{Mg}_{17}\text{Al}_{12}$.

Reduced approximately one third in reproduction.

twin formation, crystal habit, etch-pit characteristics can be examined in detail. In this way information beyond that so far possible by other techniques may be gained.

The appearance of slip is illustrated in Fig. 6. The micrograph shows a pure magnesium specimen, as cast, etched, then squeezed in a vice, with no further treatment of the surface. True slip lines are

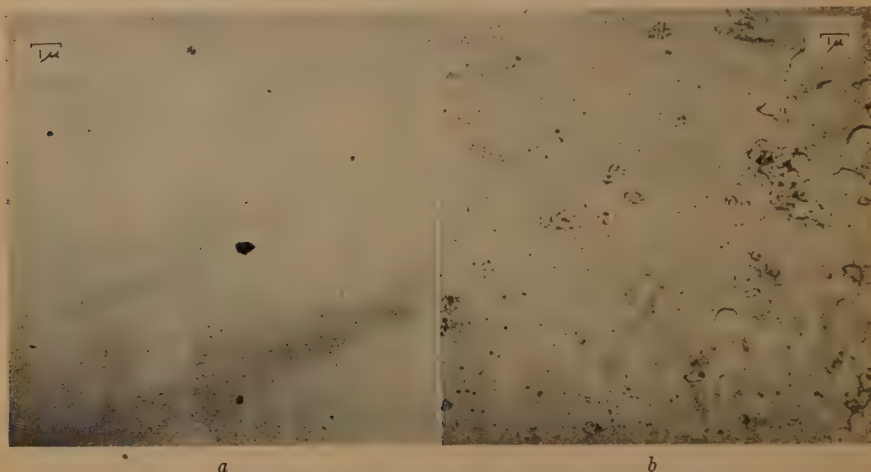


FIG. 4.—HIGH-PURITY AND COMMERCIAL CELL MAGNESIUM:

a. Distilled magnesium crystal. Original magnification 6500.

b. Commercial cell magnesium with inclusions indicating impurities (0.02 per cent Fe, 0.05 Mn). Original magnification 5500.

Reduced approximately one-third in reproduction.

Fig. 4a illustrates a crystal of distilled magnesium with only negligible impurities detectable by spectroscopic analysis. The black spot in the center is a dust particle, useful for focusing. Even in this pure magnesium, however, there is some faint structure in the center. Fig. 4b is an electron micrograph of normal commercial cell magnesium, containing 0.002 per cent Al, 0.001 Cu, 0.02 Fe, 0.05 Mn, 0.003 Si and 0.001 Cd, Ni, Sn and Zn. The effect of these normally contained impurities on the microstructure is apparent.

In Fig. 5 is shown the unetched surface of a single crystal of magnesium grown by condensation of the vapor. Great care was taken to avoid working the crystal, nevertheless it is possible that the prominent lines are slip lines. On the other hand, the lines could be evidence of growth characteristics of magnesium, possibly traces of the basal plane.

visible in only one of the three crystallites. The wavy lines in one of the grains are due not to slip, but to the etch attack.

A striking picture of twins in a single crystal of a Mg + 1.5 per cent Mn alloy is shown in Fig. 7. An interesting feature is a discontinuous change of direction on one side of a twin band, but an apparently continuous change on the other side.

Fig. 8 is another electron micrograph of a single crystal of Mg + 1.5 per cent Mn alloy, this time showing precipitation. X-ray diffraction indicated that the normal to the surface shown is 8° from the pole of the basal plane. Thus, precipitation is occurring on the basal plane, along the three principal directions.

Fig. 9 is of a Mg + 6 per cent Al alloy in the heat-treated and quenched condition. For some unknown reason a crystallographic etch pattern was produced. This pattern is not obtained if any precipitation

has occurred. An interesting feature of this picture is the manner in which the two grains merge into one another.

from solid solution. It may be expected that initial stages in the precipitation process can be observed, that directional effects

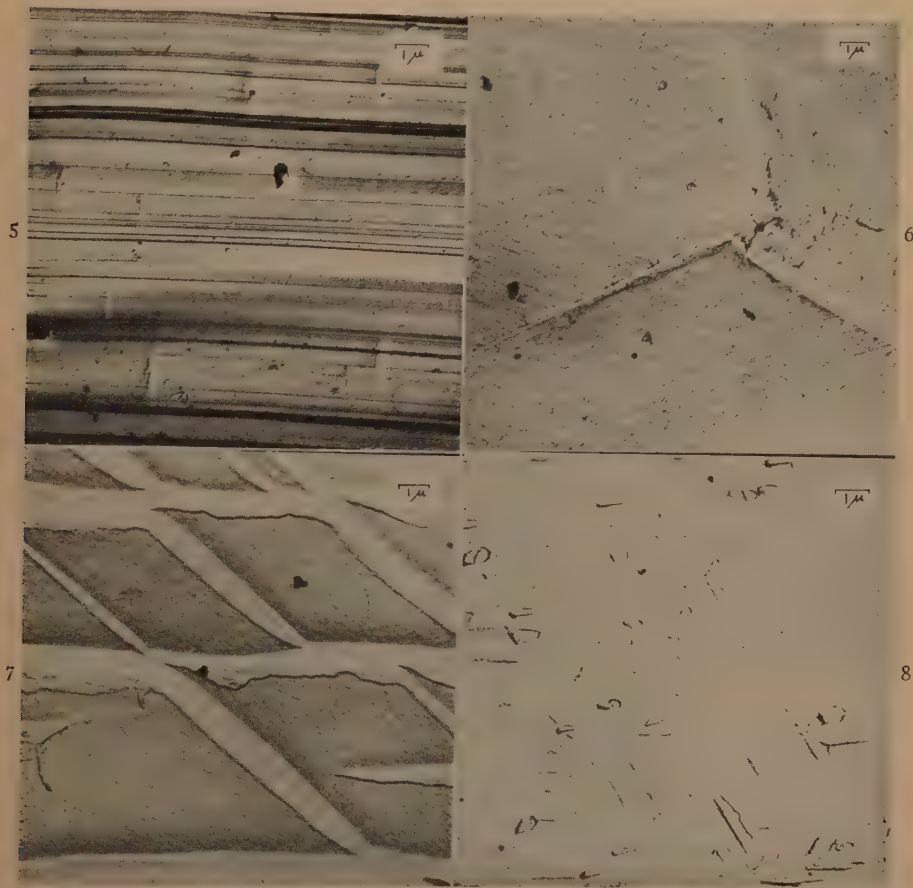


FIG. 5.—UNETCHED SURFACE OF MAGNESIUM CRYSTAL CONDENSED FROM THE VAPOR STATE.

Lines may be due to either slip or growth characteristics in the crystal. Original magnification 6500; reduced approximately one third in reproduction.

FIG. 6.—SLIP LINES IN PURE MAGNESIUM, AS CAST.

Specimen deformed in compression after etching with true slip lines appearing in the lower crystal only. Original magnification 6000; reduced approximately one-third in reproduction.

FIG. 7.—TWINS IN A SINGLE CRYSTAL OF AN ALLOY OF MAGNESIUM PLUS 1.5 PER CENT MANGANESE. Original magnification 6000; reduced approximately one-third in reproduction.

FIG. 8.—PRECIPITATION IN A SINGLE CRYSTAL OF AN ALLOY OF MAGNESIUM PLUS 1.5 PER CENT MANGANESE.

The precipitation occurs as plate-shaped particles on the basal plane along the three principal directions. Original magnification 7000; reduced approximately one third in reproduction.

Types of Precipitation

A second basic field for careful study by electron microscope technique is that of precipitation of second-phase material

may be clearly defined and that structure within the precipitated particles themselves may be found.

One example of striking orientation of

precipitation in a Mg + 1.5 per cent Mn alloy was given in Fig. 8. In general, three distinct types of precipitation are found in

+ 1.5 per cent Mn alloy, as cast. In the light microscope, they appear as random dots, not resolvable particles. Note the

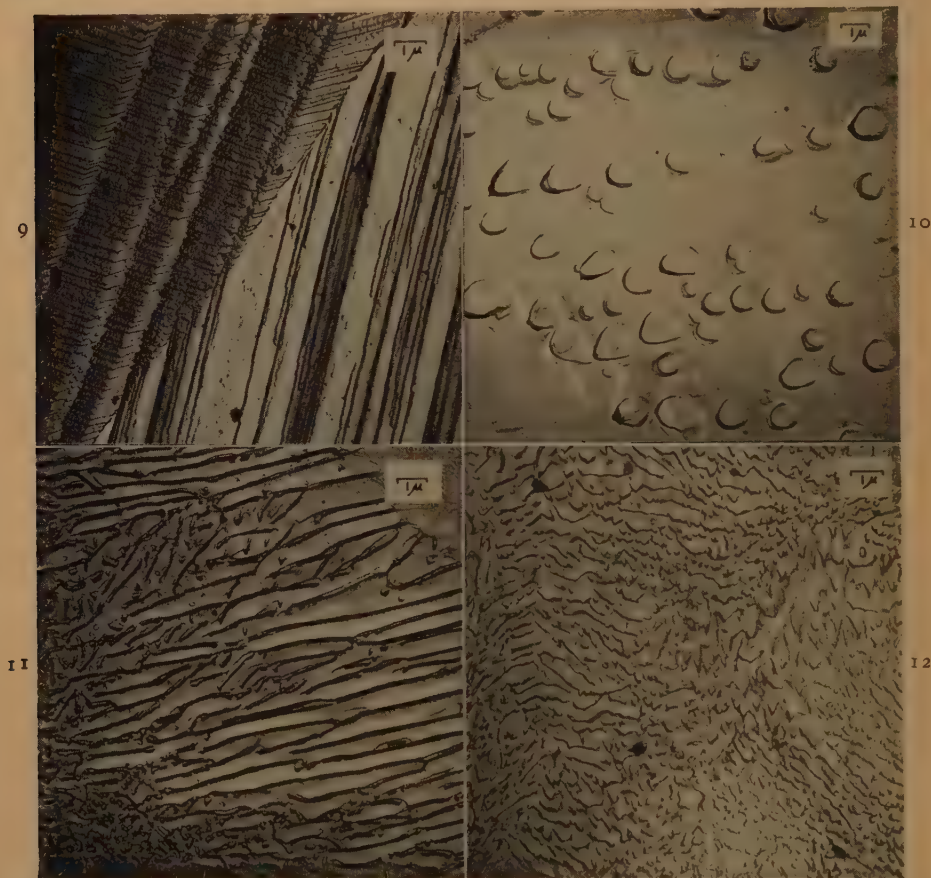


FIG. 9.—CRYSTALLOGRAPHIC ETCH ATTACK IN A SOLID SOLUTION OF MAGNESIUM PLUS 6 PER CENT ALUMINUM.

Original magnification 6500; reduced approximately one third in reproduction.

FIG. 10.—GLOBULAR PARTICLE PRECIPITATION IN AN ALLOY OF MAGNESIUM PLUS 1.5 PER CENT MANGANESE AS CAST.

The presence of such particles as these is evident in the light microscope but they cannot be individually resolved. Original magnification 5500; reduced approximately one third in reproduction.

FIG. 11.—COARSE LAMELLAR PRECIPITATION IN AN AGED ALLOY OF MAGNESIUM PLUS 10 PER CENT ALUMINUM.

Original magnification 6000; reduced approximately one third in reproduction.

FIG. 12.—FINE LAMELLAR PRECIPITATION IN AN AGED ALLOY OF MAGNESIUM PLUS 7 PER CENT ALUMINUM AND 3 PER CENT ZINC.

Original magnification 6500; reduced approximately one third in reproduction.

magnesium alloys. The first of these (Fig. 10) is a series of globules appearing at random throughout the grain in a Mg

structure within the particles. Several stages of coagulation of two or more particles are also present.

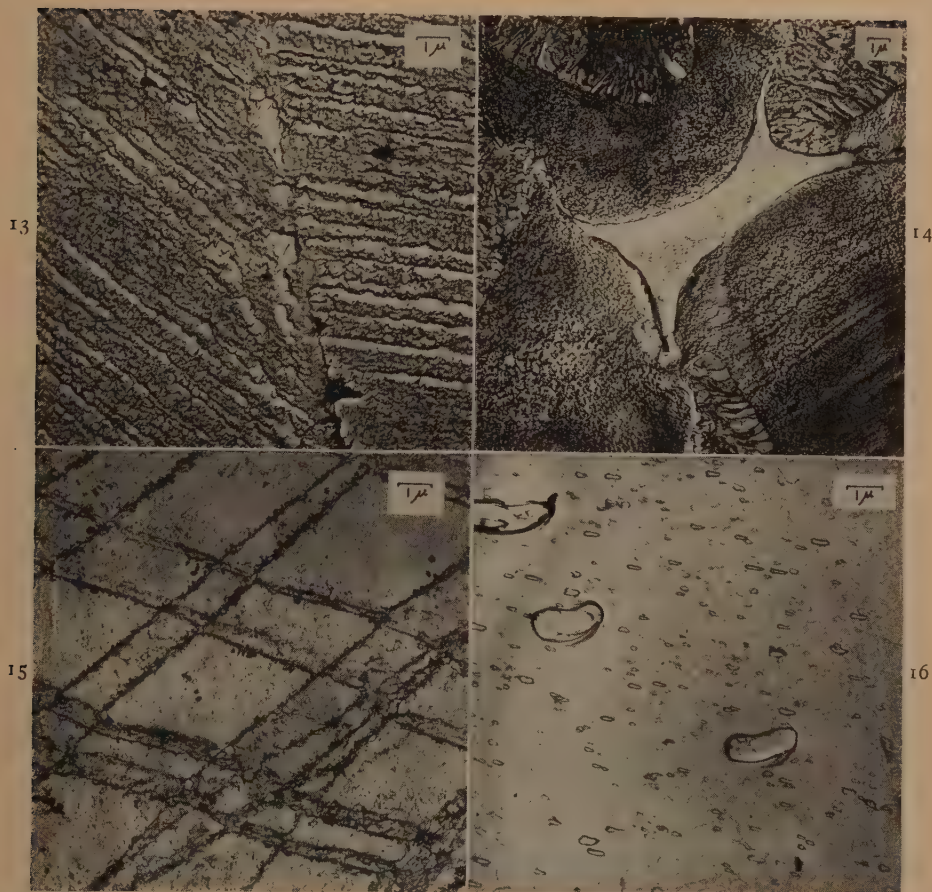


FIG. 13.—WIDMANSTÄTTEN TYPE PRECIPITATION IN AN AGED ALLOY OF MAGNESIUM PLUS 3 PER CENT ALUMINUM AND 7 PER CENT ZINC.

The directional platelike particles change direction at a grain boundary. Original magnification 6500; reduced approximately one third in reproduction.

FIG. 14.—HEAT-TREATED, QUENCHED AND AGED ALLOY OF MAGNESIUM PLUS 9 PER CENT ALUMINUM, 2 PER CENT ZINC AND 0.2 MANGANESE.

A massive piece of undissolved $Mg_{17}Al_{12}$ with surrounding Widmanstätten type precipitation and beds of lamellar precipitation. Original magnification 4500; reduced approximately one third in reproduction.

FIG. 15.—CROSS-ROLLED ALLOY OF MAGNESIUM PLUS 6 PER CENT ALUMINUM, 1 PER CENT ZINC AND 0.2 PER CENT MANGANESE, AFTER AGING, SHOWING TWINNING AND VERY FINE PRECIPITATION.

Small black globular particles widely scattered over the surface are presumably actual particles of $Mg_{17}Al_{12}$ transferred from the metal specimen to the silica replica. Figs. 20 and 21 are further examples of this phenomenon. Original magnification 6500; reduced approximately one third in reproduction.

FIG. 16.—GLOBULAR PARTICLE PRECIPITATION IN A ROLLED ALLOY OF MAGNESIUM PLUS 1.5 PER CENT MANGANESE PLUS 0.3 PER CENT CERIUM.

Scattered coarse particles are resolvable with the light microscope but the fine particles are completely invisible. Original magnification 7000; reduced approximately one third in reproduction.

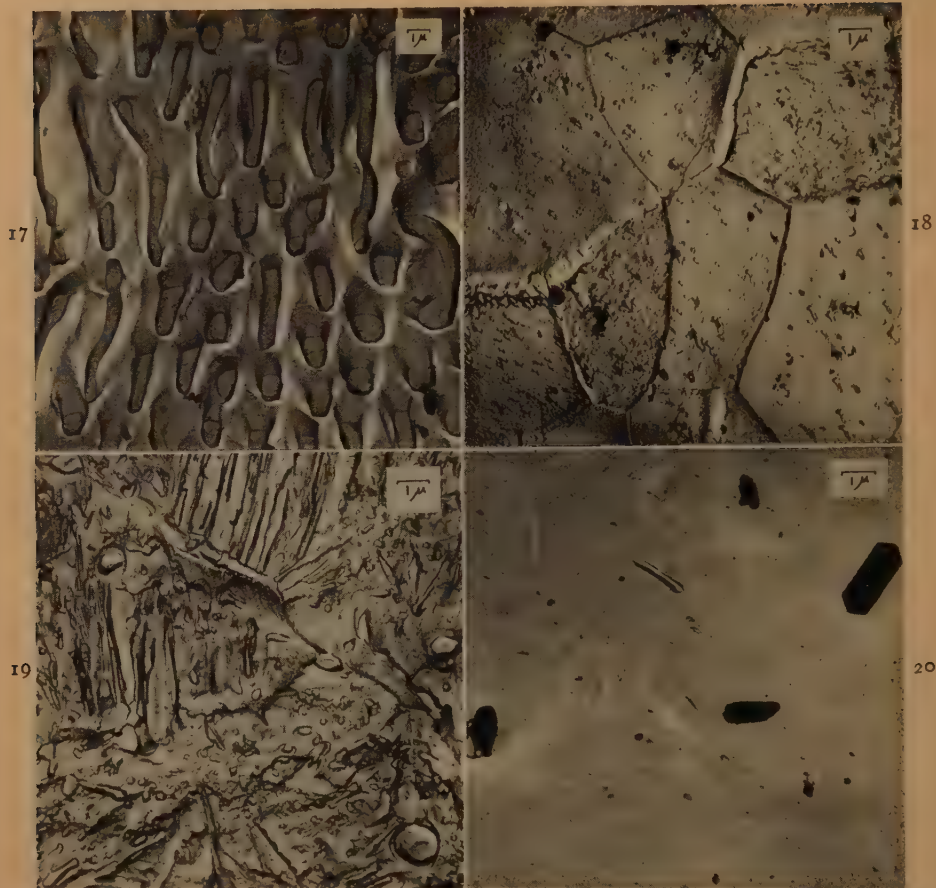


FIG. 17.—EUTECTIC STRUCTURE IN AN ALLOY OF MAGNESIUM PLUS 32.2 PER CENT ALUMINUM AS CAST.

Rodlike Mg solid solution, characteristic of this eutectic composition, has been sectioned transversely in the region shown. The circular structure thus consists of the pits from which the Mg phase has been removed by the etchant. The surrounding matrix or ridges consist of $Mg_{17}Al_{12}$. Original magnification 4500; reduced approximately one third in reproduction.

FIG. 18.—EXTRUSION OF FINE-GRAINED ALLOY OF MAGNESIUM PLUS 1.5 PER CENT MANGANESE WITH FINE PARTICLE PRECIPITATION.

Original magnification 6500; reduced approximately one third in reproduction.

FIG. 19.—HEAT-TREATED AND AGED FORGING OF AN ALLOY OF MAGNESIUM PLUS 8.5 PER CENT ALUMINUM, 0.5 PER CENT ZINC AND 0.2 PER CENT MANGANESE.

A few scattered spherical particles of massive compound may be seen with fine globular precipitation and lamellar precipitation. Original magnification 6500; reduced approximately one third in reproduction.

FIG. 20.—PURE MAGNESIUM AS CAST, WITH GRAPHITE PLATELETS ON SILICA REPLICA.

Mg containing carbon in which some of the graphite inclusions were transferred from the etched surface of the metal to the silica replica in the form of very thin platelets. Original magnification 6500; reduced approximately one third in reproduction.

A second type, lamellar precipitation, is illustrated in Fig. 11. In the light microscope, this aged Mg + 10 per cent Al alloy closely resembles pearlite and in the electron microscope it is seen to consist of a series of coarse plates. A very much finer distribution of lamellar precipitation is shown in Fig. 12. The details shown here are not resolvable, of course, in the light microscope.

A third type of precipitation is a Widmanstätten arrangement of particles, appearing in the light microscope as parallel lines within a grain. Their appearance in the electron microscope (Fig. 13) from an aged Mg + 3 per cent Al + 7 Zn alloy is a series of platelike particles, ordered in direction within a given grain, and changing this direction at a grain boundary.

Some Common Structures

Fig. 14 is of an alloy of Mg + 9 per cent Al + 2 Zn + 0.2 Mn, in the heat-treated, quenched, and aged state. A piece of massive, undissolved $Mg_{17}Al_{12}$, Widmanstätten precipitation and pearlitic-type precipitation are all shown. The similarity between this electron micrograph and a light micrograph is striking.

An alloy of Mg + 6 per cent Al + 1 Zn + 0.2 Mn cross-rolled and aged is illustrated in Fig. 15, showing twinning and some fine precipitation within the twins.

A heavily cold-rolled Mg + 1.5 per cent Mn + 0.3 Ce alloy is shown in Fig. 16. A few large particles and many small ones are visible. This micrograph is interesting because it reveals the small particles that are invisible with the light microscope.

The appearance of a eutectic is given in Fig. 17, which shows a Mg + 32.2 per cent Al alloy, as cast. There is a pronounced three-dimensional effect in this electron micrograph, with the $Mg_{17}Al_{12}$ standing in relief. The Mg phase has been etched away, leaving the deep pits between the $Mg_{17}Al_{12}$ ridges.

An example of a very fine-grained metal is given in Fig. 18, representing Mg + 1.5 per cent Mn alloy extrusion. Very fine particle precipitation is also exhibited.

The appearance of a forging of an alloy of Mg + 8.5 per cent Al + 0.5 Zn + 0.2 Mn heat-treated and aged is shown in Fig. 19. A great deal of detail is shown, none of which is clearly evident in the light microscope. Globular precipitation, lamellar precipitation, and some massive compound are all present.

Special Micrographs and Techniques

During the course of research on a variety of subjects using the electron microscope, a number of interesting specialized techniques were developed. Most of these emphasize the importance of close collaboration among various investigational methods for obtaining maximum results. Examples of the most interesting of these techniques are given.

Occasionally a small inclusion in the metal sample will stick to the polystyrene replica and then be transferred to the silica replica. When this happens, the inclusion itself, rather than a replica of the inclusion, is seen in the microscope. A striking example of this is shown in Fig. 20, of a replica of a magnesium sample containing carbon. Electron diffraction studies of the silica replica revealed that the dark platelets are graphite. Apparently flakes of free graphite were suspended in the melt before freezing.

Another example of the same effect is shown in Fig. 21, a Mg + 5 per cent Ni alloy hot-rolled + cold-rolled + aged. In this electron micrograph, transferred inclusions of Mg_2Ni and replicas of the same inclusions are seen. The faithfulness of reproduction of the shape of the inclusions is readily seen.

An interesting use of the methyl iodide etchant is illustrated in Fig. 22, showing a Mg + 6 per cent Al + Be alloy. The sample was taken from the bottom of a billet, where

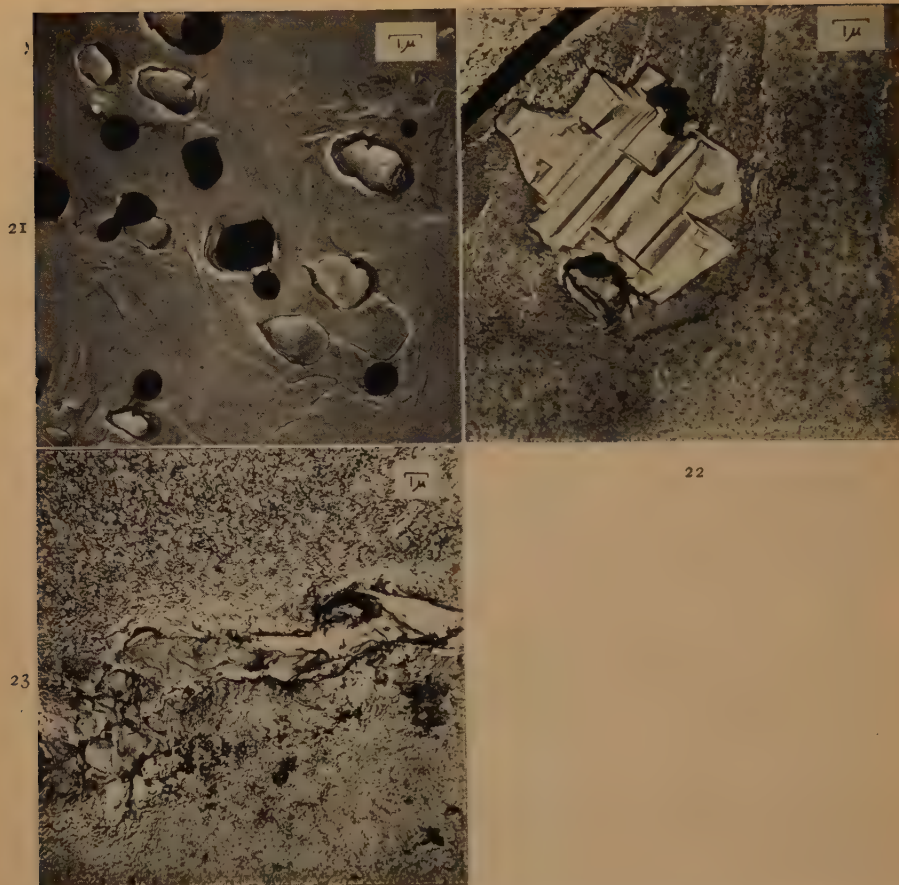


FIG. 21.—ALLOY OF MAGNESIUM PLUS 5 PER CENT NICKEL, HOT-ROLLED + COLD ROLLED + AGED, WITH GLOBULAR PARTICLES OF Mg_2Ni ON THE SILICA REPLICA.

This micrograph not only shows a replica of the globular Mg_2Ni particles but also the actual particles themselves on the silica replica. The faithfulness of the replica technique in reproducing the size and shape of the particles is evident.

Faint grain boundaries appear in the background, showing the alloy to have very fine grains. Original magnification 6500; reduced approximately one third in reproduction.

FIG. 22.—MASSIVE PARTICLE OF BERYLLIUM IN AS-CAST ALLOY OF MAGNESIUM PLUS 6 PER CENT ALUMINUM PLUS BERYLLIUM.

Illustrates preferential etch attack of methyl iodide etchant. This particle has been only very slightly attacked by the etchant. Original magnification 7000; reduced approximately one third in reproduction.

FIG. 23.—STRESS-CORROSION CRACK IN ANNEALED SHEET OF ALLOY OF MAGNESIUM PLUS 3 PER CENT ALUMINUM, 1 PER CENT ZINC AND 0.3 PER CENT MANGANESE.

This alloy was etched following the laboratory stress-corrosion cracking. The replica shows the side walls of this very minute transcrystalline crack. Original magnification 4500; reduced approximately one third in reproduction.

most of the beryllium had settled. The particle shown in the figure stands in bold relief with very little attack by the etchant. These particles were in such sharp relief

A further fruitful field of application appeared to be that concerned with solid solutions and pre-precipitation phenomena. At least one class of age-hardening alloys

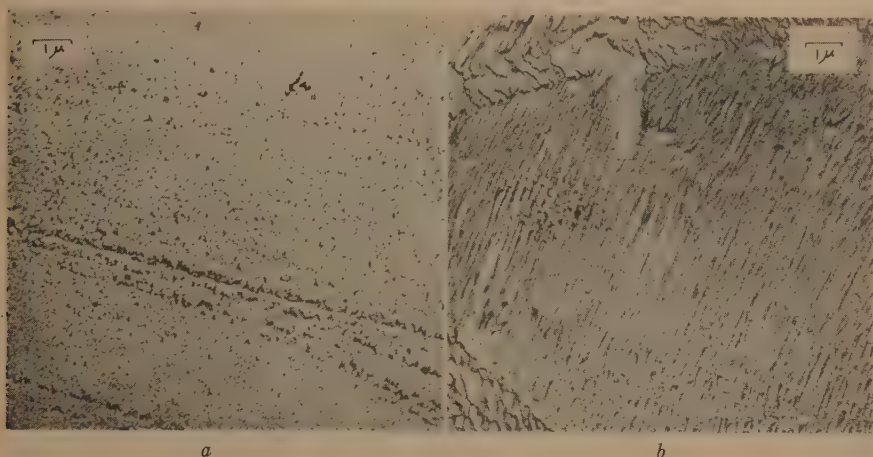


FIG. 24.—SOLID SOLUTION OF MAGNESIUM PLUS 5 PER CENT ALUMINUM.

a. Conventional metallographic polish and glycol etch. Structure is independent of composition of the solid solution. Electron diffraction indicates the presence of a film on the metal surface.

b. Methyl iodide etch showing typical "fine structure." Electron diffraction of such a surface shows bare metal.

Original magnification 7500; reduced approximately one third in reproduction.

that it was found possible to scrape a sufficient quantity of them from the surface, using a low-power microscope for viewing, to obtain X-ray diffraction, spectroscopic and chemical analyses.

Fig. 23 is a replica of a stress-corrosion crack in a sheet of Mg + 3 per cent Al + 1 per cent Zn + 0.3 per cent Mn alloy. The metal structure along the vertical edge of the crack can be seen. This technique is useful in examining minutely the immediate region of failure and, together with correlated work found in the following pages, has aided in an understanding of the stress corrosion of magnesium alloys.

Structure of Mg-Al Solid Solutions

The previous sections have covered the more or less usual microstructures and have shown that the methyl iodide etchant not only gives results that are consistent with those obtained by standard methods, but provides much additional detail.

owes its properties to the intermediate stage between complete solid solution and fully formed precipitate. The technique was therefore further developed to investigate the processes taking place when a solid solution transforms to yield a precipitated phase.

The first studies were conducted on a series of binary Mg-Al alloys ranging from 1 to 10 per cent Al. Small specimens were solution-heat-treated in helium-filled glass ampules for several days at 825°F. (440°C.) and then quenched. The electron micrographs of what were supposedly complete solid solutions always exhibited considerable etch structure, which did not have the appearance of etch figures and which was absent in pure magnesium.

A series of experiments was carried out to determine the cause of this structure. It was found first that the structure (termed "fine structure" for want of a better name) was obtained only with the methyl iodide

etchant. If ordinary etchants such as glycol, nital, hydrochloric acid, acetic acid, acetic picral, or an electrolytic polish are used, no difference in the detailed microstructures of solid solutions of different properties is noted, even though (Fig. 3) gross phases are still found for other states. Fig. 24 shows a comparison between a normal metallographic polish and glycol etch and the methyl iodide etch on a Mg + 5 per cent Al solid solution. The structure in the glycol-etched sample of Fig. 24a is now known to be due to a surface film and is independent of the composition of the solid solution. "Fine structure" and other details of similar magnitude observed in Fig. 24b are lost.

The following possible explanations for the "fine structure" were experimentally tested:

1. Peculiarity of the methyl iodide etch attack.
2. Precipitation of $Mg_{17}Al_{12}$.
3. Formation of Guinier-Preston zones.
4. Stresses resulting from the quench.
5. A transformation similar to that of the formation of martensite in steel.
6. Preferential segregations of impurity atoms.

All of these possibilities were satisfactorily eliminated except the last, and it was finally concluded that an impurity or impurities were responsible for the "fine structure." From complete analyses of the specimens and consideration of the atomic radii of the impurity metals present, iron was suggested as a possibility, since it was common to all of the samples in which the structure was observed. Further, stress-corrosion results with commercial alloys indicated that the alloys that exhibited the "fine structure" were more susceptible to stress corrosion. The influence of iron on the corrosion behavior of magnesium is well known.

More evidence was desired, however, and a series of alloys of varying compositions was prepared in order to ascertain the

effect of both composition and heat-treatment. These alloys were prepared, using sublimed magnesium crystals and Super Purity aluminum. The results for two alloys containing Mg + 6 per cent Al but different iron contents are shown in Fig. 25. The far greater intensity of "fine structure" in the 0.021 per cent Fe alloy as compared with that with 0.001 per cent Fe may be presumed to be due to an iron phase, and has been confirmed many times.

The effect of actual precipitation of $Mg_{17}Al_{12}$ on the "fine structure" was rather illuminating. A specimen of an alloy of Mg + 6 per cent Al + 1 Zn + 0.2 Mn was solution-heat-treated at 825°F. (440°C.) and quenched to yield the structure shown in Fig. 26a. A similar specimen cut from the same sheet was furnace-cooled from 825°F. (440°C.) to yield a precipitate of $Mg_{17}Al_{12}$ particles shown in Fig. 26b. Another specimen from the same sheet was quenched from 825°F. (440°C.), cold-worked by 10 per cent reduction in rolling and then aged 3 hr. at 480°F. (250°C.) (Fig. 26c). It is evident that the precipitation $Mg_{17}Al_{12}$ in this alloy has eliminated the "fine structure" from the solid solution. The conclusion is that the impurity is much more soluble in the compound and has concentrated there. (Direct experiment shows iron to be much more soluble in $Mg_{17}Al_{12}$ than in pure magnesium.) If the precipitated specimen is again solution-heat-treated and quenched, the "fine structure" is again observed (Fig. 26d), so that the cycle is completed.

Further evidence of the preference of aluminum over magnesium for iron was obtained by electron diffraction studies of a series of evaporated films. The films were prepared by evaporating simultaneously the metals Fe, Mg and Al onto a silica substrate to form a mixed crystal film. When such a film is heat-treated in vacuum, it is found from the diffraction patterns that the iron interacts with the aluminum to form FeAl (or $FeAl_3$) but no $Mg_{17}Al_{12}$.

is found when the amount of iron is high. If iron is absent, $\text{Mg}_{17}\text{Al}_{12}$ is formed. Apparently the mixture $\text{FeAl} + \text{Mg}$ is more stable than $\text{Fe} + \text{Mg}_{17}\text{Al}_{12}$. An ex-

take up sufficient aluminum to form a compound, leaving only the excess aluminum to form $\text{Mg}_{17}\text{Al}_{12}$.

With these results in mind, Fe and Al

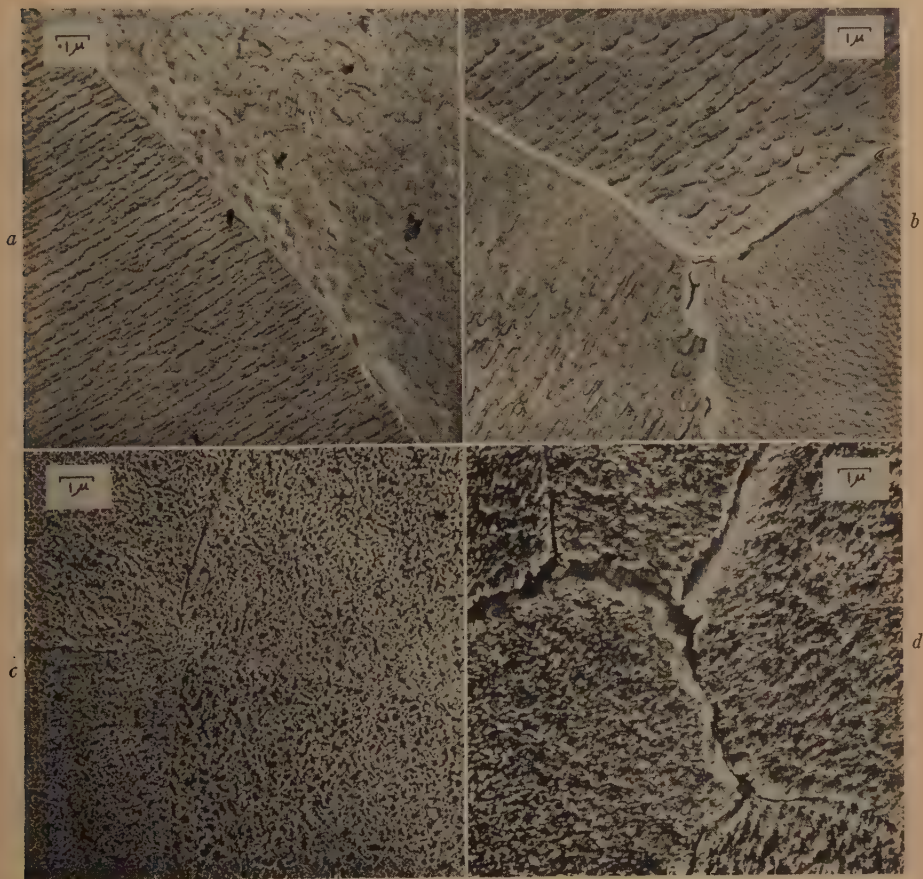


FIG. 25.—EFFECT OF IRON CONTENT ON "FINE STRUCTURE" IN MAGNESIUM PLUS 6 PER CENT ALUMINUM.

Low iron, 0.001 per cent.

a. Solution-heat-treated and water-quenched.

b. Solution-heat-treated and furnace-cooled.

High iron, 0.021 per cent.

c. Solution-heat-treated and water-quenched.

d. Solution-heat-treated and furnace-cooled.

Original magnification 6500; reduced approximately one third in reproduction.

periment in which a piece of iron was dissolved in molten $\text{Mg}_{17}\text{Al}_{12}$ corroborated this, for large crystals of FeAl could be isolated from the alloy. In the presence of both magnesium and aluminum, iron will

were evaporated simultaneously onto an etched magnesium single crystal and the specimen was then heat-treated in vacuum to bring about diffusion. This surface was etched successively deeper and electron

diffraction patterns and micrographs were obtained at various depths through the diffusion zone. The appearance of the surface at a depth where a pattern for both

However, the electron diffraction pattern obtained from the diffusion zone was a spot pattern for magnesium with rings for FeAl. The actual "fine structure" in the alloys



FIG. 26.—EFFECT OF $Mg_{17}Al_{12}$ PRECIPITATION ON "FINE STRUCTURE" IN AN ALLOY OF MAGNESIUM PLUS 6 PER CENT ALUMINUM, 1 PER CENT ZINC AND 0.2 PER CENT MANGANESE.

a. Solution-heat-treated at 825°F. and quenched, showing considerable "fine structure."
b. Solution-heat-treated at 825°F. and furnace-cooled. $Mg_{17}Al_{12}$ particles are observed with the "fine structure" greatly diminished.

c. Solution-heat-treated at 825°F. and quenched to give "fine structure" and then cold-worked and aged. $Mg_{17}Al_{12}$ particles are evident with little "fine structure."

d. Aged sample from c, showing little "fine structure," is again solution-heat-treated at 825°F. and quenched. "Fine structure" has returned with the solution of the $Mg_{17}Al_{12}$.

Original magnification 6000; reduced approximately one third in reproduction.

magnesium and FeAl was obtained is shown in Fig. 27. The similarity between this structure and that found in a solution-heat-treated and quenched Mg + 6 per cent Al binary (Fig. 28) is pointed out.

always gives a ring pattern for magnesium along with rings that agree with the FeAl spacings. Not enough lines are obtained for positive identification as FeAl in this case.

However, electron diffraction examination of a large number of alloys containing "fine structure" has yielded the conclusion that the pattern developed is consistent

Examination of a large number of alloys has indicated that the presence of both iron and aluminum in magnesium is required to produce the "fine structure." In



FIG. 27.

FIG. 27.—SYNTHESIZED "FINE STRUCTURE."

Iron and aluminum were evaporated simultaneously onto a magnesium single crystal and heat-treated to bring about diffusion. The specimen was then etched into the diffusion zone. Electron diffraction showed both magnesium and FeAl present. Note similarity in the "fine structure" here and that observed in Fig. 28. Original magnification 6500; reduced approximately one third in reproduction.



FIG. 28.

FIG. 28.—SOLID SOLUTION OF MAGNESIUM AND 6 PER CENT ALUMINUM.

Original magnification 7000; reduced approximately one third in reproduction.

with FeAl. The present conception of this structure is, then, that it consists of a segregation of FeAl,* perhaps along flaws or boundaries between mosaic blocks of the magnesium crystal. This segregation has often changed the magnesium diffractions from single-crystal spots to a ring pattern, indicating that the magnesium crystal is partially fragmented as a result. X-ray patterns from large-grained specimens will give single-crystal patterns indicating that only a small portion of the magnesium crystal is fragmented. This is doubtless in the regions near the FeAl deposits. Further work on the details of the structure is called for not only through fundamental interest but from a practical viewpoint as well.

* The term FeAl here includes any iron-aluminum compound isomorphous with FeAl.

the absence of aluminum, the structure is not found unless the iron content is very high. Systematic investigations of the aluminum-iron ratio for which the structure occurs have not been undertaken. In a single series, however, the structure was absent for aluminum contents up to 0.15 per cent. At 0.53 per cent Al the structure was quite evident and increased in density up through 1 per cent. This series will be discussed in the next section.

That the "fine structure" discovered in the magnesium-aluminum alloys is quite important from a practical standpoint will be shown in the next section. The great sensitivity of the electron microscope and electron diffraction to minute amounts of impurities is emphasized by this work. The selectivity of the methyl iodide etchant makes this type of analysis possible.

CORRELATION OF "FINE STRUCTURE" WITH CORROSION PROPERTIES

The etch structure and conclusions regarding its origin discussed in the foregoing pages are not only of fundamental

The corrosion of magnesium-aluminum alloys has been quite extensively studied⁹ as regards the effects of certain impurities such as iron, nickel and copper. The general conclusion has been that when the impurity

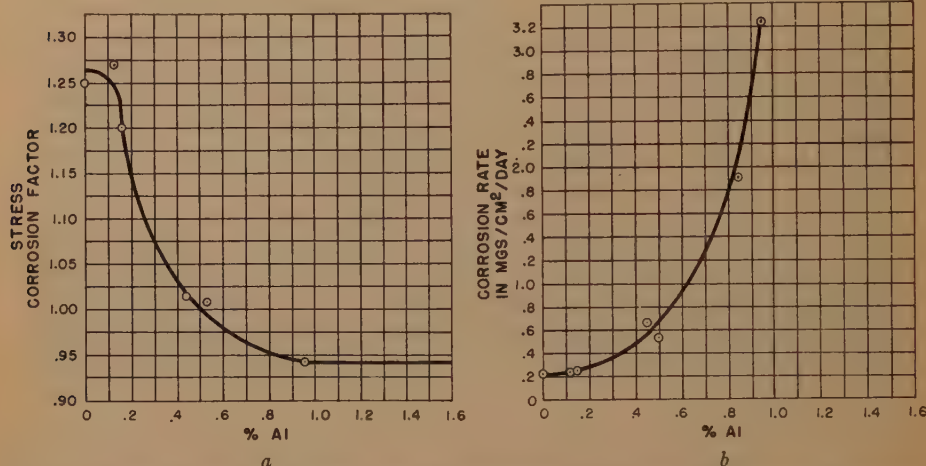


FIG. 29.—RELATIONSHIP BETWEEN STRESS-CORROSION FACTOR, GENERAL CORROSION RATE AND ALUMINUM CONTENT.

a. Stress-corrosion factor is defined as the ratio of stress for failure in salt chromate solution to the yield stress. Sharp increase in stress-corrosion sensitivity between 0.15 and 0.53 per cent Al correlates with the threshold of "fine structure" as observed in Fig. 30.

b. Corrosion rate, (mg. per sq. cm. per day) in 3 per cent salt water. Correlation can also be observed between the increasing corrosion rate above 0.15 and 0.53 per cent Al and the presence of "fine structure" as observed in Fig. 30.

interest but prove to bear a close relation to the corrosion properties of magnesium alloys. This relation was indicated before any work concerning its origin had been done. It was first observed in alloys of Mg + 6 per cent Al + 1 Zn + 0.2 Mn that were being tested for accelerated stress-corrosion properties. When it became apparent that there might be such a correlation, a program was undertaken to investigate the possibilities. This paper is concerned chiefly with metallography and any detailed consideration of corrosion is not warranted. However, sufficient corrosion data will be included to illustrate the importance of the electron microscope and electron diffraction findings in this connection.

content exceeds a "tolerance limit" (about 0.002 per cent for iron) a discontinuity occurs in the corrosion-composition curves beyond which the corrosion rate is much greater than it is below. The increased corrosion was correlated with a critical number of discrete particles of an iron phase serving as cathodes during corrosion.

A second conclusion in the work of Hanawalt and his collaborators^{9,10} was that even below the "tolerance limit" residual impurities still control the corrosion process. However, the concept of discrete particles of an iron phase was believed to be inadequate to explain stress-corrosion behavior, since several alloys with iron contents well below the "tolerance limits" were found to be quite

susceptible to stress cracking. It was considered that the transgranular "fine structure" may well represent the manner in which the residual impurities are dis-

In Fig. 29a the "stress-corrosion factor" (defined as the ratio of stress for failure in salt-chromate solution to the yield stress) is plotted against aluminum content below

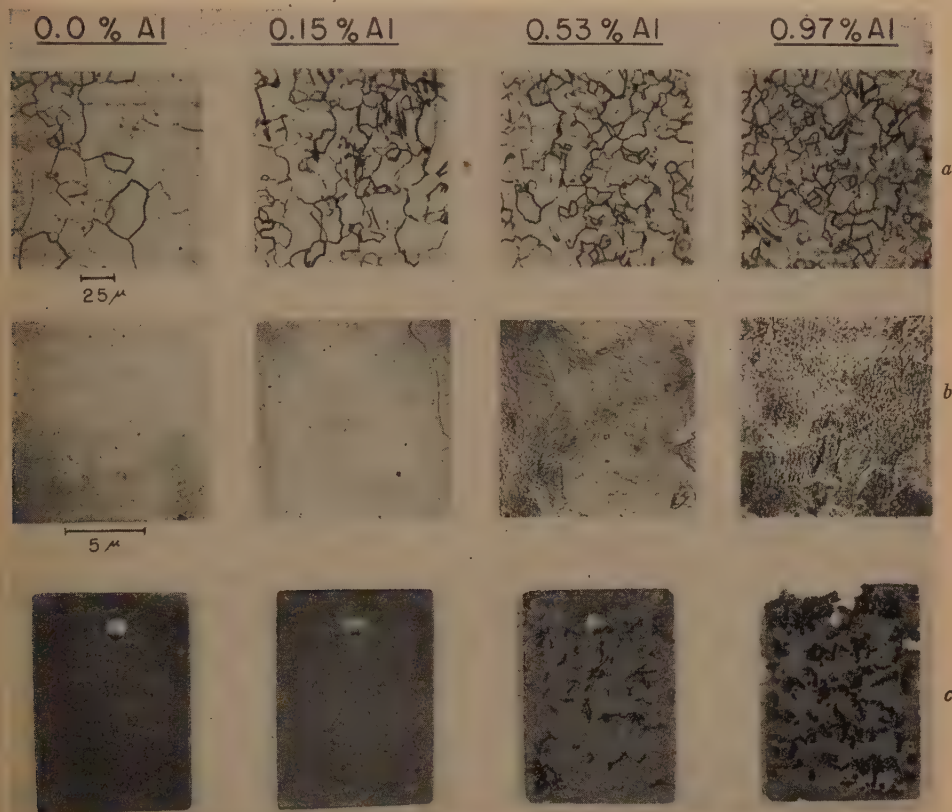


FIG. 30.—COMPOSITE OF LIGHT MICROGRAPHS, ELECTRON MICROGRAPHS, AND GENERAL CORROSION SPECIMENS OF ALLOYS OF MAGNESIUM PLUS 0.0 TO 1.0 PER CENT ALUMINUM.

Note correlation between "fine structure" in electron micrographs of the 0.53 and 0.97 per cent Al alloys and the high corrosion rate of the corresponding metal specimens in 3 per cent salt water.

a, light micrographs; *b*, electron micrographs; *c*, general corrosion samples.

tributed. Such a dispersion could account for the typical transcrystalline stress-corrosion cracks observed in wrought Mg-Al alloys.

The corrosion data* are conveniently summarized for one particular series of Mg-Al binary alloys by Fig. 29a and 29b.

* A full report of the methods and results will appear in a separate paper. The effect of heat-treatment is of considerable importance in considering corrosion results.

the solid solubility limit of aluminum in magnesium. Fig. 29b shows the general corrosion rate in 3 per cent salt water as a function of aluminum content for this same series of alloys. All of the impurities Fe, Ni, Cu, Mn were present to less than 0.001 per cent each.

Fig. 30 is a composite showing light micrographs, electron micrographs and the general corrosion specimens of this same

series. Close examination of the light micrographs yields nothing that can account for the corrosion behavior. The electron micrographs, however, indicate the onset of the "fine structure" above 0.15 per cent Al. The threshold is difficult to determine, but is certainly somewhere between 0.15 and 0.53 per cent Al in this series. The effect of the "fine structure" on the general corrosion is strikingly shown by the pronounced pit attack, or "worm tracks," in the corrosion specimens (Fig. 30). The effect on stress corrosion is quite evident in Fig. 29a.

It is concluded from this and other similar data that the presence of the "fine structure" is a large factor in the corrosion behavior of magnesium-aluminum alloys with iron contents below the tolerance limit.

The iron content alone, however, is not sufficient, but requires a minimum of aluminum in order to produce the structure. The solution potential differences between iron-aluminum compounds and the matrix⁹ are very much greater than between $Mg_{17}Al_{12}$ and the solid solution. Further, the precipitation of $Mg_{17}Al_{12}$ has been found to decrease the stress-corrosion susceptibility and general corrosion rate in accordance with the behavior of "fine structure" upon heat-treatment, as described in the previous section.

In addition to the corrosion results, it has been observed that magnesium-aluminum alloys exhibiting "fine structure" tarnish much more rapidly than do alloys in which the structure is absent. The tarnishing reaction has not been sufficiently well investigated to lead to any conclusions as to reaction products in the two cases.

There are many questions to be investigated concerning the occurrence of the "fine structure" and the physical and chemical behavior of the alloys. The importance of structures not detected by

light microscopic and X-ray methods is clearly demonstrated and it is possible that such investigations should prove fruitful in many alloy systems.

SUMMARY

1. A new etching (methyl iodide) and rinse procedure has been developed for magnesium alloys, which yields, in contrast to standard etchants, a surface free of films and mechanical distortion.

2. The surface resulting from this etchant may be examined in the electron microscope by use of the polystyrene-silica replica technique, or by reflection electron diffraction methods.

3. The methyl iodide etchant gives, in the electron microscope, results that are not only consistent with those observed in the light microscope, but also much additional detail.

4. In a study of magnesium-aluminum solid solutions, a new dispersion of an iron-aluminum phase has been discovered. This dispersion, called "fine structure," is important in understanding both stress and general corrosion processes for magnesium-aluminum alloys of controlled purity.

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"Shadow-cast" Replicas for Use in the Electron Microscope

BY HELMUT THIELSCH*

(Chicago Meeting, February 1946)

METALLOGRAPHIC specimens whose surfaces are to be investigated are too thick to allow either light or electrons to pass through them for microexamination by transmission. This difficulty is overcome with optical microscopes by illuminating the surface through the objective lens. For electron microscopes best results are obtained by preparing thin replicas of the surface of the specimen, placing them in the microscope and passing the electron beam through them.

Since electron microscopes represent a rather recent invention, they have found little application as compared with optical microscopes. This is true because, aside from the cost of new equipment and development of new techniques, some of the older replica methods necessitated the destruction of the surface from which a thin transparent replica was obtained. In other processes in which the surface is preserved, either too tedious a procedure is required, unsuited to "mass-production" requirements of industrial laboratories, or replicas of insufficient contrast and sharpness are produced.

In general, investigations with the electron microscope involve five steps: (1) polishing the surface of the metal specimen, (2) proper etching of the surface, (3) preparing the suitable replica from the

surface, (4) examination and photography in electron microscope and (5) interpretation.

PREPARATION OF METAL SURFACES

Usual metallographic polishing is generally satisfactory. It is important though that the final polish be applied very carefully, since otherwise evidence of a small amount of deformation might show up even on relatively deeply etched surfaces. A high-power microscope should be used to determine the suitability of the polish and etch. This, of course, is not different from optical examinations, but in these, if a deep etch is used, the problem is less serious.

It is frequently difficult to detect with optical microscopes poor polishing aside from superficial scratches before etching. Figs. 1 and 2 show micrographs of "well" and "poorly" polished nickel etched by immersing the sample for 20 min. in a solution containing 8 grams cupric sulphate in 40 c.c. of concentrated HCl and 40 c.c. of H₂O (Marble's reagent). The sample shown in Fig. 1 was polished in its final stages for 5 min. on a carborundum wheel followed by 10 min. on a rouge wheel. whereas the sample shown in Fig. 2 was polished only 1 min. on the rouge wheel. Generally, this procedure does not guarantee that the surface of the specimen will be either undistorted or deformed. It was applied here merely to show the effects of good and poor polishing. To the experienced investigator, plastic deformation is

Manuscript received at the office of the Institute June 22, 1945; revised Dec. 20, 1945. Issued as T.P. 1977 in METALS TECHNOLOGY, February 1946.

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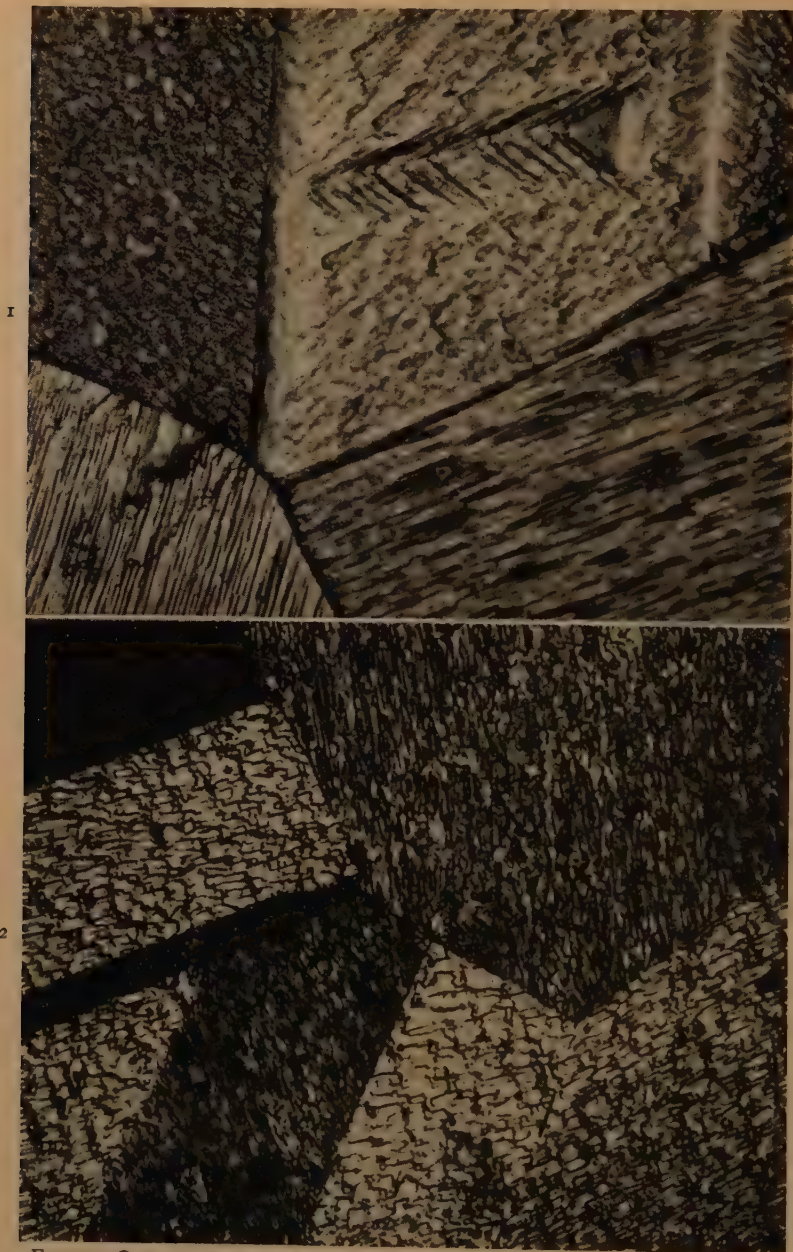


FIG. 1.—OPTICAL MICROGRAPH OF WELL-POLISHED NICKEL SPECIMEN. $\times 1000$.
FIG. 2.—MICROGRAPHS OF POORLY POLISHED NICKEL SPECIMEN. $\times 1000$.

visible in Fig. 2. The lamellar etching structure shown in the two bottom grains in Fig. 1 appears fragmented in similar oriented grains in Fig. 2. For comparison,

replicas from the surface will become more difficult for deeper etches. Also, if optical microscopes are used to observe the deep etches, the samples may appear there



FIG. 3.

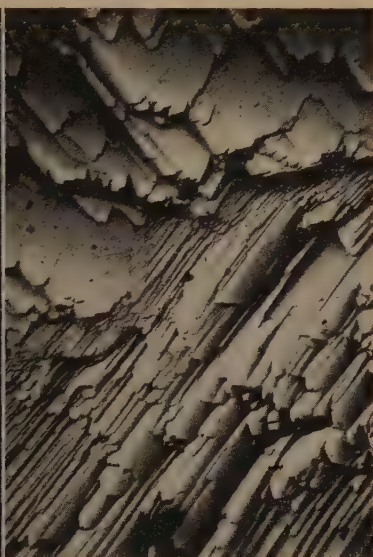


FIG. 4.

FIG. 3.—CHROMIUM SHADOW-CAST REPLICA OF PROPERLY POLISHED NICKEL SPECIMEN.

FIG. 4.—MANGANESE SHADOW-CAST REPLICA OF POORLY POLISHED NICKEL SPECIMEN.

Both $\times 5000$.

electron micrographs are shown of the same surface, though not the identical spots, in Figs. 3 and 4, respectively.

After a good polish has been obtained, the next problem is the choice of etchants and etching techniques. As is true also for optical examinations, many etches are not suitable for investigation with the electron microscope; in fact, for the latter the number of suitable etches is more limited. The reason for this lies in the development of a characteristic inner grain structure, which will be discussed in further studies.

Deeper etches will reveal to a better degree the grain and inner grain structures of the metals. Thus it is often advisable to double or even triple the etching times recommended for the various solutions. On the other hand, the separation of the

"badly" overetched (Figs. 1 and 2), though in the electron microscope a "nice" structure is visible for the same etch (Figs. 3 and 4).

It is important to remember that the different etching solutions will develop different inner grain structures, since the various alkali or acid etchants differ in their attack upon the various crystallographic planes.

Thus in copper a propionic acid etch tends to produce an octahedral structure (Figs. 5 and 6) attacking the $\{111\}$ planes to a lesser degree than the $\{100\}$ planes. The 50 per cent NH_4OH (20 c.c.) — H_2O_2 (5 c.c.) etch tends to show a cubic block structure (Fig. 7) different from the lamellar cubic structure obtained with the ferric



FIG. 5.—COPPER ETCHED WITH PROPIONIC ACID (40 C.C.) — H_2O_2 (15 C.C.).

Etching time 20 minutes.

FIG. 6.—COPPER ETCHED WITH PROPIONIC ACID (40 C.C.) — H_2O_2 (15 C.C.).

Etching time 15 minutes.

FIG. 7.—COPPER ETCHED WITH 50 PER CENT NH_4OH (20 C.C.) — H_2O_2 (5 C.C.).

Etching time 60 seconds.

FIG. 8.—COPPER ETCHED WITH FeCl_2 (10 GRAMS), ALCOHOL (120 C.C.) AND HCl (30 C.C.).

Etching time 40 seconds.

All $\times 5000$.

chloride (10 grams) in alcohol (120 c.c.) and HCl (30 c.c.) etching reagent (Fig. 8).*

"SHADOW-CASTING" REPLICA TECHNIQUE

After the sample has been properly polished and etched, a thin, transparent replica is made from the surface of the metal specimen. Best results have been obtained so far with either collodion or formvar films. The first part of the method used here is essentially the same as developed by Schaefer and Harker, of the General Electric Co., and described by the authors in various papers.²⁻⁵ A replica is prepared by spreading a dilute solution of formvar or collodion in a solvent over the surface of the specimen. As the solvent evaporates a very thin film is formed, which should be thick enough to show the blue or green interference colors (i.e., not more than a few thousand Ångstrom units). Before the replica is removed from the specimen, a piece of scotch tape, upon which a 200-mesh wire screen has been placed, is then pressed firmly upon the surface of the replica. To protect the center of the wire screen from the glue of the tape, a piece of thin paper (about 2 mm. thick) is inserted between the tape and the screen. To ease the removal of the replica, it is often advisable to breathe heavily upon the specimen, as the moisture in the breath will assist in loosening the film from the metal.

This transparent replica obviously will not possess a great deal of contrast, since, being made of an organic substance, its atoms are too light to absorb or scatter effectively the electrons in the electron beam. For this reason the so-called "shadows" are deposited on the surface of the replica.

The replica is then placed into a vacuum

system for deposition of a metallic film upon the impressed surface.* There are many points in the technique that effect the quality of the image. The farther the replica is placed from the filament, the sharper the shadows will be, since then the rays will be more nearly parallel. On the other hand, more metal must be evaporated, as the thickness of the sublimed film will decrease as the square of the distance. For most evaporations an angle of replica surface to line from filament to replica of about 40° to 50° should be used, though if a very fine structure—precipitated particles, for example—is to be observed with shadows, smaller angles should be applied.

It is important that the medium used in the evaporation does not crystallize upon condensation at room temperature. Thus, most metals of high boiling points are suitable. This, of course, varies for the different metallic materials, depending upon the complexity of the crystal structure and the recrystallization point. For face-centered cubic metals, gold with a boiling point of 5371°F. represents a borderline case. Very thin films will appear structureless, though heavier deposits will give evidence of crystallization.¹² Thus the structure shown in Fig. 9 of a collodion replica of a nickel specimen (same surface

* Covering replicas with a thin film of a suitable metal is not new.⁶ For the electron microscope "shadow casting" was first reported by Muller,^{7,8} who applied the technique to measure the height of fine particles. Mahl⁹ followed with the evaporation of metallic shadows (chromium) upon surface replicas. In this country the same techniques were reported recently by Thomasson, Williams and Wyckoff.^{10,11} The various authors found that the metal film deposited by evaporation onto the replica will produce shadows of great sharpness, which will show up the surface structure of the specimen in excellent detail. This method in its present development combines most of the advantages of the previous replica techniques. The ease with which replicas may be prepared, and the detail, contrast, and sharpness, will make this "shadow-casting" method an important tool in metallographic investigations with the electron microscope requiring high magnifications and resolving power.

* For copper Glauner and Glocker¹ show the relative attacks of several etching solutions upon the various face-centered cubic planes. A similar study with the electron microscope is now in preparation.

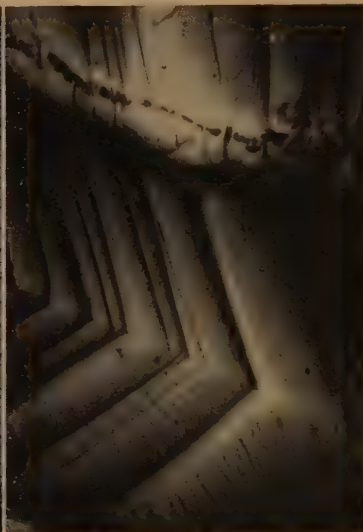
¹ References are at the end of the paper.

as in Fig. 3, though not the identical area) is due to "granulation" of the gold "shadow." Fig. 8 represents a better

may be interpreted falsely as due to strains on the surface of the original specimen.



FIG. 9.



[FIG. 10.]

FIG. 9.—GOLD SHADOW-CAST REPLICA OF NICKEL SHOWING CRYSTALLIZATION DUE TO TOO HEAVY A DEPOSIT.

FIG. 10.—CHROMIUM SHADOW UPON A WRINKLED COLLODION REPLICA OF NICKEL.
Both $\times 5000$.

(thinner) gold shadow-cast replica of a copper specimen. Even here a small amount of granulation is visible.

Body-centered cubic chromium has been used with far more success. Figs. 3, 10, and 13 represent chromium shadows.

Manganese (cubic complex, boiling point 3904°F .) has been applied by the author with best success. It produces shadows of great sharpness, and does not show evidence of crystallization even for very heavy deposits. With the exception of Figs. 3, 8, 9, 10 and 13, all electron micrographs in this report are made of manganese "shadow-cast" collodion replicas.

It is important that the replica be supported smoothly by the mesh-wire screen; otherwise the film may wrinkle and upon evaporation a shadow structure similar to that in Fig. 10 may appear. This structure

APPEARANCE OF SHADOW-CAST REPLICAS

Two factors determine the difference in blackening on the photographic plate; namely, the thickness of the replica film and the relative thickness of the shadow (thickness parallel to the electron beam).

The former is direct in that the thinner the replica the fewer electrons will be absorbed or scattered. Thus the photographic plate will receive more blackening, producing lighter areas on the print. In other words, "hills" on the original metal surface will appear on the final photographic print lighter than the "valleys."

The second factor may be defined as "the relative thickness of the shadow," and is caused by the metal film formed on the replica. Usually this one is of the greater importance. In "shadow-casting"

areas perpendicular to the path of the atoms emitted from the filament by evaporation will receive the heaviest

The *oxide layer* method developed by Mahl¹³ consists essentially of an oxide film produced electrolytically on the sur-

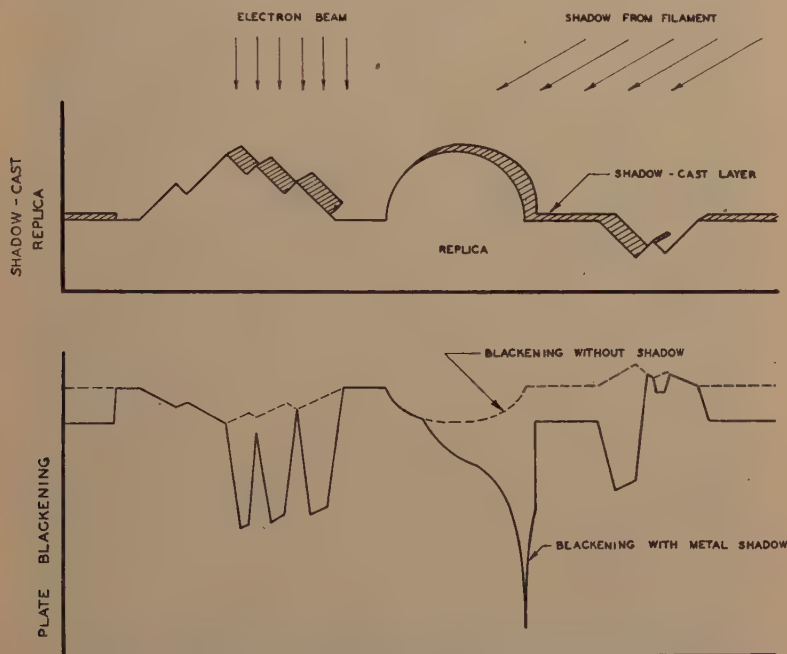


FIG. 11.—SCHEMATIC REPRESENTATION OF SHADOW-CAST REPLICA.

deposits. In Fig. 11 a schematic representation of a shadow-cast replica is given.

Figs. 12 and 13 show shadow-cast replicas of pearlite and nickel, respectively, which show clearly the white "shadows." An angle of 40° was used here in the evaporation.

Shadow-cast collodion replicas of gray cast iron and a low-carbon iron etched with ferric chloride (10 grams) in alcohol (120 c.c.) and HCl (30 c.c.) are shown in Figs. 14 and 15, respectively.

COMPARISON OF DISCUSSED TECHNIQUE WITH OLDER REPLICA METHODS

The shadow-casting technique was developed in order to overcome many of the disadvantages and shortcomings of the previous methods, which will be discussed in the following paragraphs.

face of the metal. Since mercury does not attack metallic oxides, this film may be removed by immersing the specimen in mercury or mercuric chloride.¹⁴ When the surface is scratched, the mercury penetrates between the metal and its oxide layer and lifts up the latter. This method has been applied successfully so far only on aluminum, for which very good electron micrographs have been shown by a variety of investigators. Since this method necessitates the destruction of the original surface, it has not been widely accepted.

Another method, also developed by Mahl, has until recently been popular in Germany. In this method, a thin lacquer or collodion film is formed on the surface of the specimen. At first this replica was removed by dissolving the metal.⁹ Since this again required the destruction of



FIG. 12.—SHADOW-CAST REPLICA OF PEARLITE.

FIG. 13.—SHADOW-CAST REPLICA OF NICKEL.

Compare etching blocks with micrograph of same sample in Fig. 1.

FIG. 14.—SHADOW-CAST REPLICA OF GRAY CAST IRON.

FIG. 15.—SHADOW-CAST REPLICA OF LOW-CARBON IRON SHOWING CARBIDES AND INNER GRAIN ETCHING STRUCTURE.

All $\times 5000$.

the surface, Mahl lately has improved his method by removing the replica electrolytically.¹⁵

To show this, the copper sample etched with propionic acid (Figs. 5 and 6) was subjected to the molding process just



FIG. 16.



FIG. 17.

FIG. 16.—SHADOW-CAST REPLICA OF COPPER, OF WHICH A POLYSTYRENE MOLD HAD BEEN MADE.
FIG. 17.—SHADOW-CAST REPLICA OF COPPER, OF WHICH A POLYSTYRENE MOLD HAD BEEN MADE.
Both $\times 5000$.

The formvar method perfected by Schaefer and Harker²⁻⁵ consists of forming a formvar or collodion film on the surface of the specimen and removing this film by immersion in water or by various other stripping processes. A lack of sufficiently high contrast and sharpness often make it difficult to interpret electron micrographs prepared by this formvar method.

In this country the polystyrene-silica method of Heidenreich and Pack¹⁶ has so far been used in most studies, since with it replicas of great sharpness, detail, and contrast are produced. As this method requires a molding process at a temperature of close to 150°C . and about 3000 lb. per sq. in. pressure, a small amount of surface deformation and oxidation may appear on many electron micrographs. Unfortunately, previous authors so far have neglected to consider these effects.

described. Manganese shadow-cast replicas were then made of the copper surface (Figs. 16 and 17). Deformation and oxidation is clearly recognizable. Since, in addition, this process is on the whole rather tedious, it may lose its present importance.

Good results may also be obtained with the silver-collodion process,^{17,18} which again, besides being rather tedious, lacks the contrast and sharpness obtained with the shadow-casting technique. In this process a silver layer is built up on the surface of the specimen by evaporation in a vacuum. After the layer has been removed from the surface, a collodion film is spread over the silver replica and the latter is then dissolved in weak nitric acid, which does not attack the collodion. The collodion replica is studied in the electron microscope.

CONCLUSION

Comparison of the electron micrographs shown in this report with those obtained by previous authors and shown in the references mentioned shows the advantage of this new "shadow-casting" process. Not only does this method produce replicas of high contrast and sharpness, but the short time required for preparation of the replicas will make this method an easy and quick approach to detailed metallographic investigations.

ACKNOWLEDGMENT

This research was made possible by a grant-in-aid from the Horace H. Rackham Trust Fund. Valuable suggestions by Dr. R. Schneidewindt and Dr. L. Thomasson made the final conclusion of this report possible. Dr. D. L. Katz generously allowed time from one of his electron microscopic projects to be used for this investigation.

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DISCUSSION

(C. S. Barrett presiding)

C. H. GEROULD.*—I would like to take a moment to consider our polystyrene-silica replica technique, which was developed at the Dow Chemical Co. and which was mentioned in the paper just given by Mr. Thielsch. He stated that he feared that our replica technique would cause difficulty due to deformation of the metal as a result of the application of pressure during the molding process.

We at the Dow have never had any reason to suspect that any deformation of the metal was occurring during the molding process. Our procedure has been to heat the polystyrene to a temperature of 160°C. before applying any pressure, at which temperature the polystyrene is a viscous liquid. By so doing the pressure of the polystyrene against the metal is essentially hydraulic and is therefore applied equally in all directions, which we feel should not cause deformation.

Our work using this replica technique has brought forth several indications that deformation of the specimen is negligible. These indications are:

* The Dow Chemical Co., Midland, Michigan.

1. Direct comparisons have been made between the light and electron microscopes when studying a specific spot on a metal surface. These "same spot" studies were obtained by first taking micrographs at high magnification, with a light microscope, of a specific structure that could be readily recognized. Silica replicas were then prepared in the conventional manner using a pressure molding and the same spot was located and photographed in the electron microscope. When these micrographs were enlarged to the same magnification, the differences observed were largely due to differences in resolution of the two instruments. Particle sizes and shapes were the same.

2. Silica replicas of metals have been obtained using pressures varying from a few pounds per square inch up to such excessive pressures as 5000 lb. per sq. in. without visible differences showing up in the electron microscope that would indicate distortion of the metal.

3. A 15,000 lines per inch diffraction grating ruled in speculum metal has been used repeatedly in making silica replicas. A particular section of the grating has been pressure-molded upward of 50 separate times using pressures between 1000 and 2000 lb. per sq. in. without any changes in the surface contours or dimensions of the grating being observable when the silica replicas were checked in the electron microscope. Deformation of the metal during a single molding must be negligible in such a case.

4. A variation of the polystyrene-silica replica technique has been developed and studied at the Dow. This variation eliminates the bulk pressure molding of polystyrene, replacing it with a heavy polystyrene-lacquer coating. In this case the impression is formed entirely by the wetting of the specimen surface by the lacquer, no pressures being applied. This technique gives results that are almost

identical with those of the bulk molding process, except where very fine structures (200Å. or less) are involved.

H. THIELSCH (author's reply).—I did not intend to discuss in detail the merits or disadvantages of the polystyrene-silica process, for it is true that there are certain applications that are handled advantageously by the polystyrene-silica method. To name a few examples: certain types of (deeply) etched surfaces make the removal of collodion films extremely difficult, if not impossible, but allow the separation of the polystyrene impression. Thus, I have made successful studies on etched anthracite coal, extremely deep etched iron and other samples with the polystyrene-silica process, but at times have been unable to do so with the collodion shadow-casting technique. Similarly, certain corroded surfaces may necessitate the "Heidenreich" process.

In regard to Mr. Gerould's statements I should like to say that light microscopes, because of their relatively poor resolving power, hardly reveal the "inner grain" structures, and thus comparison of photographs made of the same spot with light and electron microscopes does not show the evidence of "non-deformation" as suggested by Mr. Gerould. Therefore, the "same-spot" comparisons generally are referred only to grain-structure outlines. Also, most of the earlier studies on microscopic-electron microscopic comparisons published by Dr. Heidenreich and co-workers were made on hard-surfaced metallurgical specimens such as steel. On such samples, of course, distortion will be evidenced to a lesser degree than on softer materials. Moreover, no comparisons have been made so far by Dr. Heidenreich or his co-workers between this method and the shadow-casting technique. This has been done in the laboratories at the University of Michigan.

Lamellar and Mosaic Structures—X-ray and Thermodynamic Evidence

BY HELMUT THIELSCH,* STUDENT ASSOCIATE A.I.M.E.

(New York Meeting, October 1945)

DURING the last three decades a great many arguments have been presented on the subject of "mosaic" or "block" structures of metals. Apparently because of insufficient evidence, the "block-structure" theories have never been widely understood among the physical metallurgists in this country, and most investigators among the few that have tried to demonstrate the existence of such an inner structure of crystals or grains have failed to recognize also the existence of a lamellar structure. Moreover, little thought has been given to justify the existence of such "lamellar" or "mosaic-block" structures on a theoretical basis.

Since properties such as plasticity, ferromagnetism, hardness, diffusion, and others may be explained by structural faults in the lattice network of the crystals, the great importance of a more detailed knowledge of the structure within crystals or grains becomes now evident.

Because of the vast extent of the field of submicroscopic structures, it shall be the purpose of this paper only to review the more important of the results obtained by other investigators, especially in Germany, where a great deal of attention has been given to mosaic structure during the last three years. The origin of this mosaic pattern† and effects of cold reduction and

recrystallization will be shown in further studies later on.

IMPERFECTIONS IN CRYSTALS

The many terms used in the literature to denote structural types of crystals are often not clearly defined. To clear up some of the confusion, the meaning of the more important terms will be given here.

Ideal, or Perfect Crystals.—Crystals without any structural imperfections are called "ideal crystals," or "perfect crystals," meaning a homogeneous interior structure of atoms, ions or molecules, as the case may be. In other words, at every point in the interior of the crystal exactly the same orientation of the crystallographic axes of the coordinate system would exist. The surface of such a body, if etched with an appropriate etching reagent, would reflect light with perfect uniformity. Crystals of this type are almost nonexistent.

Real Crystals.—"Real crystals"¹ may contain various types of structural defects, which can be classified into: (1) lineage structure, (2) mosaic-block structure, (3) lamellar structure. The inhomogeneities existing in these groups mean that the orientation of the crystallographic axes will not be the same at every point within the interior of a crystal (or grain of a polycrystalline body).

Perfect Real Crystals.—The term "perfect real crystals" is generally used to describe crystals with minute structural or thermodynamical inhomogeneities. The former

Manuscript received at the office of the Institute April 25, 1945. Issued as T.P. 1931 in METALS TECHNOLOGY, October 1945.

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† Throughout the paper the words "mosaic pattern" will signify both the lamellar and mosaic-block structure.

¹ References are at the end of the paper.

defect, of the order of 10^{-7} to 10^{-8} cm., consists of foreign atoms or missing atoms within the lattice pattern of the crystal (Smekal's "Locker-Stellen"^{2,3}). The thermodynamic inhomogeneity consists of variations and disturbances in the vibrations of the atoms or ions (see also p. 51). Experimentally it was first observed and discussed by Becker⁴ and Orowan,^{5,6} who noted changes in shear strength with changes in temperature for various materials. Neither of these imperfections necessitates differences in the orientation of the crystallographic axes, and thus has no bearing upon the position of X-ray diffraction patterns, though the latter will cause effects upon diffuse spots of Laue photographs. Because of their small magnitude, electron micrographs show no evidence of either of these minute structural and thermodynamic imperfections.

Lineage Structure (Fig. 1), discussed in great detail by Buerger,⁷ is well known, since it can be detected relatively easily by microscopic methods, by which it is shown as badly distorted Laue spots. Its origin is in the irregularities formed during the growth of dendrites. The size of the disorder varies between 10^{-1} and 10^{-4} centimeters.

The *Mosaic-block Structure* differs from the lineage structure quantitatively only in size, since for various materials the blocks vary between 10^{-3} and 10^{-7} cm. These blocks are orientated only relatively parallel with fluctuations in the alignment up to about 10° min. Between the blocks the regular atomic network is disturbed, and external influences such as mechanical and temperature treatments have a bearing upon the "perfection" of the mosaic inner-grain structure.

The block and lineage structures have often been confused with one another. Actually the two types of imperfections are independent of each other, and may even appear simultaneously.⁸

Some indications point toward the possibility that the mosaic-block structure is of

secondary nature; i.e., due to relief of stresses set up during solidification, or even more directly due to recrystallization of deformed materials.*^{9,10} Other indica-

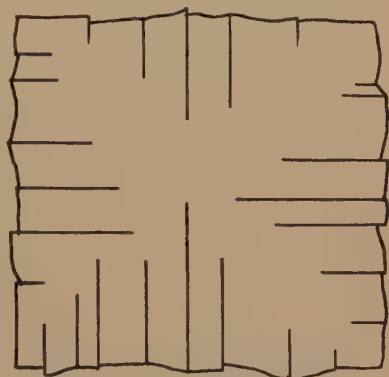


FIG. 1.—LINEAGE STRUCTURE.

tions of this are given in a series of papers published by Dehlinger,¹¹ Dehlinger and Gisen¹² and Gisen,¹³ in which the authors show that recrystallized metals have a certain definite shear strength that is absent in cast materials. In other words, much lower shear stresses are necessary to deform cast crystals than are required for the deformation of recrystallized crystals. The authors' interpretation that recrystallized metals possess an intrinsically stronger mosaic structure than cast metals can also be applied to the belief that mosaic crystals are of secondary nature.

Lamellar Structure seems to be of primary nature. The distance between the lamellae varies from 10^{-4} to 10^{-6} cm. This structure is generally found in crystals formed by slow cooling, by sublimation or by electrodeposition.

As yet information regarding the origin of both the lamellar and mosaic-block structures is incomplete and many more carefully planned experiments should be

* This does not imply that any recrystallized metal will have a mosaic-block structure. In a later paper, electron micrographs of samples of nickel and Chromel will be shown, which exhibit typical lamellar structures, even though the metals have been drawn and recrystallized.

made. It can be regarded as certain that foreign atoms, even in small amounts,^{3,14} and cooling rates^{15,16,17} will be the main decisive factors determining the primary inner-grain structure and its dimensions.

Almost nothing is known about the nature of the atomic network on the interfaces between the blocks or lamellae, though knowledge here would seem important to the study and understanding of the process of plastic deformation and recrystallization.

Since it is the purpose of this paper to clarify the various controversial concepts of mosaic-block and lamellar structures, only those two will be discussed here.

METHODS OF INVESTIGATION

Various methods have been employed by a multitude of authors to prove (or disprove) the existence of a mosaic structure. The more important and conclusive of these methods are:

1. X-ray Spectroscopic Evidence.
2. Thermodynamic Approach.
3. Microscopic Evidence.*
 - a. Etched Surfaces of Polished Materials.
 - b. Unetched Surfaces of Cast Metals.
 - c. Other Microscopic Methods.
4. Electron Microscopic Evidence.*

X-ray Spectroscopic Evidence

So far most of the evidence of mosaic structure has been advanced by investigators in the field of X-ray diffraction. From results first published by Mosely and Darwin,^{18,19,20} differences in the width of arc and intensity of reflected lines were noted between the values obtained for most crystals and for some of the few perfect real crystals.²¹ Theoretical calculations made for ideal crystals will predict diffracted lines 3 to 6 sec. of arc in width, whereas experi-

mentally almost all single crystals (real crystals) will give lines as much as several minutes in arc width. Some difficulty exists here from the fact that the change in width of the diffracted lines will decrease with increase in the size of blocks and will disappear at about 10^{-5} cm. Thus for larger block sizes proofs have been based mainly upon intensity calculations²² where the difference between the values obtained from actual measurement and the theoretical values amounts to a factor of 10 or more.

A certain amount of background scattering is due to the thermal agitation of the atoms within the crystal (see p. 51), yet the diffuse scattering actually measured on Laue photographs greatly exceeds the predicted value by Laue-Bragg reflections. Only the mosaic-structure inhomogeneity can account for such discrepancies.

Many other investigators²³⁻³¹ have reported various observations for a score of crystals, a description of which would be beyond the scope of this paper.

The average size of the mosaic blocks differs for different materials,* being somewhat smaller for metals, where the upper limit of block size lies probably near 10^{-4} cm: For salt crystals larger sizes have been reported. Renniger⁸ measured for NaCl block sizes up to 10^{-1} cm. Of course, single blocks, being of uniform atomic orientation, will behave quite like perfect real crystals. Consequently, each individual block should reflect in agreement with the dynamic theory.³² Unfortunately, as Laue³³ has pointed out, owing to inexact primary extinction, the limit of the dynamic theory lies somewhat between 10^{-3} and 10^{-4} cm. Thus the error in block-size determinations will decrease to a considerable degree the

* Because of the greater length of a report on microscopic and electron microscopic evidence, those two subjects will be discussed in a separate paper.

* It is doubtful that the dimensions of the mosaic structure are an inherent property of the materials. Probably the conditions present at the moment of primary crystallization and somewhat secondary effects of reduction and recrystallization will be the main determining factor.

value of accurate investigation for blocks below 10^{-3} cm.

Because of these difficulties only a few calculations on metals have been prepared. Applying corrections to the extinction coefficient, James, Brindley, and Woods³⁴ were the first to make a quantitative study of aluminum. Recently actual values have been determined for zinc by Zehender and Kochendörfer,³⁵ who describe a somewhat improved method using monochromatic Cu- K_{α} radiation. These authors show in their paper that the size of the mosaic blocks is larger for cast than for recrystallized crystals; thus for cast zinc they obtained an average block size of from 3×10^{-5} cm. to at least 8.5×10^{-5} cm., whereas in the recrystallized state a size of about 2.7×10^{-5} cm. was found.

Preston,³⁶ studying the aging of aluminum containing 4 per cent Cu, observed on diffraction photographs numerous streaks, which showed changes in intensity as hardening continued. His explanation that this effect is due to segregation of copper atoms into thin plates,* seems reasonable and gives some experimental indication of lamellar growth.

It is unfortunate that it is rather difficult, often not even possible, to make more detailed studies, using the present known X-ray diffraction techniques. Until better methods have been developed and many more papers have been presented, the results described herein can merely be called evidence—not proof.

Thermodynamic Approach

Various attempts to correlate mosaic structure with thermodynamic equilibria or forces have been rather unsuccessful. Theories advanced by Zwicky, that mosaic crystals³⁷⁻⁴⁰ are of a more stable form than ideal crystals, are based mainly upon theoretical postulations. The many ob-

jections raised by different investigators⁴¹⁻⁴⁵ discouraged any further attempts. Thus, as it is also admitted now by Zwicky,⁴⁶ it is just as impossible to derive a stability "proof" for the fundamental necessity of a mosaic structure as it is impossible to prove the stability (or instability) of an ideal structure within crystals.

On the other hand, the thermal vibrations ascribed to the atoms are independent of structural imperfections, since they are evidenced in crystals that do not show structural faults also.

Results recently published by Lonsdale and Smith,⁴⁷ Darwin,⁴⁸ W. L. Bragg,⁴⁹ W. H. Bragg^{50, 51} and Born and Sarginson⁵² indicate such thermal effects. Thus Lonsdale, Smith and Preston show for Al, NaCl, MgO, and other materials, changes in intensity of diffuse Laue spots that increase as the temperature of the crystals is raised and decrease with a lowering of the temperature. At liquid-air temperature, these diffuse patterns seem to disappear altogether. Laval,⁵³ studying the diffuse regions produced by various crystals, found that for diamond the diffuse pattern is of smallest extent, though it will increase with increases in temperature. Lonsdale,⁵⁴ extending the investigation on diamond, introduced two types of reflections, primary and secondary, which she ascribes as due to temperature and structure-sensitive properties of the crystal, respectively. Bragg⁵¹ reports that a few predicted diffuse spots do not appear, a fact that he explains is caused when a sufficient number of small crystal groups act independently of each other within the crystal.

ACKNOWLEDGMENT

I wish to express my appreciation to Professors R. Schneidewind and L. Thomasson for their helpful discussions and constructive criticisms in the preparation of this paper.

* Similar observations were reported in several microscopic investigations, which will be reviewed in a later paper.

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DISCUSSION

(R. M. Brick presiding)

A. REIS.*—The author has given a very good survey of existing methods and data. I would like to add just a word of critical discussion of existing methods and mention one method that just has now become available.

X-ray diffraction methods give evidence about the imperfections of crystallites in two ways; that is, from intensity data and from geometric data.

Intensity data work in a way that polycrystalline materials made from very perfect grains give less intensity than so-called mosaic or lineage structure. The reasons for that can easily be made evident, but I will not take the time to discuss that.

It is not easy to draw quantitative conclusions from intensity data because imperfections of crystallites can, in certain cases, decrease intensities, and the result of imperfections upon the intensities is difficult to evaluate. With intensity data alone, we cannot draw conclusions that are quite positive.

We are much better off with geometric

evidence. Excellent geometric evidence for single crystals has been obtained in many countries by outstanding physical laboratories. DuMont, in Pasadena, has made important observations, and so have many others.

So for single crystals there is no difficulty. We can take a rocking curve on a Bragg spectrometer and its width will give an exact measurement. This gives the so-called angular domain of reflection.

If Bragg's law is applied to a perfect crystal we must have diffraction at one exact angle and the slightest deviation from that angle must make the diffraction disappear.

In fact, there is a certain angular domain of reflection that gives an exact measurement of the geometric size of the imperfections. So far, we have no way of obtaining geometric evidence on polycrystalline materials, and these are what the metallurgist is interested in.

A number of years ago I devised a method to apply that geometric way of determining imperfections to polycrystalline materials. I had the honor of having an instrument constructed according to my method in the laboratories of the General Electric Co. in Schenectady, under the supervision of Dr. David Harker, who made a wonderful precision instrument, which is now in my possession.

During the war, I had no opportunity to start those experiments. Earlier, in Paris, I had such an improvised instrument, which was given to me, and before the war started, I could just confirm that the method worked, but I could not use it on materials. I believe it will be very interesting to see how large these imperfections are in cast materials and in recrystallized materials and in many others.

I may add one individual point. About ten years ago, some metallurgists and physicists in Great Britain started to try and determine fatigue before failure by studying the imperfections in the crystallites of the metal. They hoped to find the first traces of fatigue by increased imperfections.

Gough and Wood, in the National Physical Laboratory, published a paper on that in 1936. This was repeated in several other countries—Belgium, Poland, and others—but the results were inconclusive, because the diffraction method was too crude.

* Consulting Chemist.

I hope that this point can be brought to final evidence by a precise method to determine this geometric feature.

There is one thing more that I want to talk about. The geometric feature is independent of any intensity data. It gives direct evidence on this angular domain, and gives directly the angular domains of orientations of the different parts within the crystallite.

My method gives a statistical survey of

the angular domains existing in the material. When material is uniform, we will find a distribution curve of angular domains that gives one maximum. If it is partly recrystallized, we will find two maxima.

So the method can take care of all that, and I hope that the metallurgists will give me a response and send me interesting specimens, and perhaps even help me otherwise to bring my investigation under way.

Graphical Methods of Representing Some Conditions of Plasticity

BY WILLIAM MARSH BALDWIN, JR.,* JUNIOR MEMBER A.I.M.E.

(Chicago Meeting, February 1946)

Two of the most useful and important equations available to the metallurgist for the study of plastic deformation of metals are the Huber-von Mises-Hencky¹⁻³ and the St. Venant⁷⁻¹⁰ equations.

HUBER-VON MISES-HENCKY EQUATION

The Huber-von Mises-Hencky equation answers the question: When does plastic flow occur in metal that is subjected to a multi-axial stress? It occurs, according to this equation, when the three principal stresses, σ_1 , σ_2 , and σ_3 satisfy the equation:

$$(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_1 - \sigma_3)^2 = 2K^2 \quad [1]$$

*Here K is the yield strength of the material as determined in an ordinary tensile test.

If the quantities σ_1 , σ_2 , and σ_3 are assigned to the coordinates of a Cartesian three-dimensional system, this expression describes a cylinder whose axis of symmetry is inclined at equal angles to the three coordinate axes^{4,5} (Fig. 1). The radius of this cylinder is $\sqrt{\frac{2}{3}}K$.

Manuscript received at the office of the Institute Nov. 5, 1945. Issued as T.P. 1980 in METALS TECHNOLOGY, April 1946.

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† For any stress system at a given point and at a given instant of time, it can be shown that there are three mutually orthogonal planes upon which all shear stresses vanish and only normal stresses exist. The normal stresses operating on these planes are known as principal stresses, the planes are known as principal planes, and the directions in which the principal stresses operate are known as the principal directions.

¹ References are at the end of the paper.

For the purpose of simplicity, it is sometimes advantageous to ascribe the values $\sigma_1/K = s_1$, $\sigma_2/K = s_2$, $\sigma_3/K = s_3$ to the three coordinate axes instead of the principal stress alone. In this case, Eq. 1 becomes

$$(s_1 - s_2)^2 + (s_2 - s_3)^2 + (s_1 - s_3)^2 = 2 \quad [2]$$

and the radius of the cylinder becomes $\sqrt{\frac{2}{3}}$. In the latter method of representation, a point lying inside the cylinder indicates that the metal will react elastically, whereas a point lying on the cylindrical surface indicates that the metal will behave plastically.

Some of the geometric features of this cylinder are worthy of study. Let us inquire first as to what interpretation may be placed upon what we will choose to call the "circles of latitude" of the cylinder (L in Fig. 1) and the "meridians" of the cylinder (M in Fig. 1).

Circles of Latitude

Circles of latitude are formed by allowing a plane, passing perpendicular to the cylinder axis, to intersect with the cylinder. Any point, P , on this circle is presumed to have the coordinates s_1 , s_2 , and s_3 . The coordinates of the point resulting from the intersection of the plane and the cylinder axis will be a , a , and a (since the cylinder axis is equally inclined to the three coordinate axes).

Let us now pass a line through the point on the circle and the point on the axis.

The length of this line is R , the radius of the cylinder. By definition, the direction cosines of this line will be

$$\cos h = \frac{s_1 - a}{R}, \cos j = \frac{s_2 - a}{R}, \text{ and} \\ \cos k = \frac{s_3 - a}{R} \quad [3]$$

Since the cylinder axis is equally inclined to the three coordinate axes, the following

But because of Eq. 4 this expression reduces to

$$\cos h + \cos j + \cos k = 0$$

Substituting Eq. 3 in this expression yields;

$$\frac{s_1 - a}{R} + \frac{s_2 - a}{R} + \frac{s_3 - a}{R} = 0$$

$$\text{or} \quad s_1 + s_2 + s_3 = 3a = \text{constant} \quad [5]$$

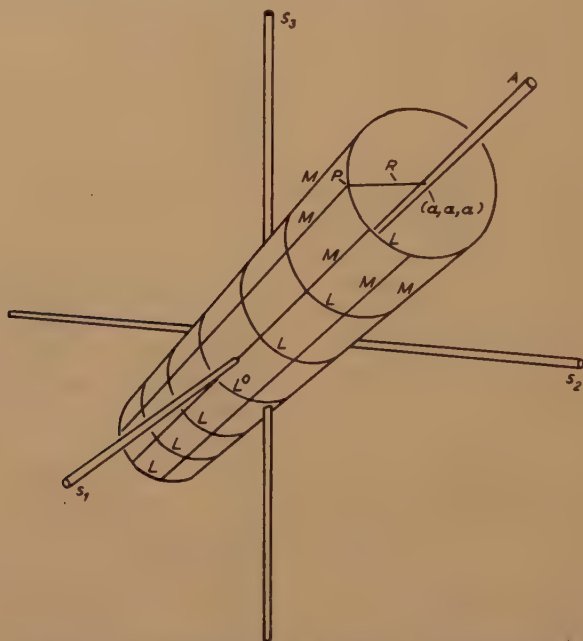


FIG. 1.—GRAPHICAL REPRESENTATION OF HUBER-VON MISES-HENCKY EQUATION.

Eqs. 1 and 2 are the equations of a cylinder whose axis A is equally inclined to the three coordinate axes s_1 , s_2 , and s_3 . The circles of latitude formed by the intersection of planes normal to the axis A with the cylinder are labeled L . The circle of latitude labelled L^0 is formed in the special case where the plane normal to the axis A passes through the origin of the Cartesian coordinate system. The meridians, which are straight lines on the cylindrical surface running parallel to the axis A , are labeled M .

expression for its direction cosines may be written;

$$\cos l = \cos m = \cos n \quad [4]$$

Now the line in question is perpendicular to the cylinder axis, so we may write:

$$\cos h \cdot \cos l + \cos j \cdot \cos m + \cos k \cdot \cos n = 0$$

Thus, the "circles of latitude" may be interpreted as the loci of points for which the sum of the principal stresses is a constant. A special case exists for the circle of latitude formed by the intersection of the cylinder and a plane passing not only perpendicular to the cylinder axis but also through the origin of the coordinate system. We shall call this circle of latitude

"the reference circle of latitude." In this case a reduces to zero and

$$s_1^0 + s_2^0 + s_3^0 = 0 \quad [6]$$

Here, s_1^0 , s_2^0 , and s_3^0 may be considered to be components of a vector passing through the origin of the coordinate system and a point on the reference circle of latitude.

Meridians

Meridians are straight lines lying in the cylindrical surface running parallel to the cylindrical axis. Let us consider a single meridian, and further presume that this meridian passes through the reference circle of latitude at a point whose coordinates are s_1^0 , s_2^0 and s_3^0 .^{*} Any other point on the meridian is assumed to have the coordinates s_1 , s_2 , and s_3 .

Because the meridian is parallel to the cylinder axis, its direction cosines will be the same as those of the cylinder axis; hence Eq. (4) will hold. Since the direction cosines of the meridian are known, and since it passes through a point whose coordinates are known, the equation for the meridian may be written:

$$\frac{s_1 - s_1^0}{\cos l} = \frac{s_2 - s_2^0}{\cos m} = \frac{s_3 - s_3^0}{\cos n}$$

or, in view of Eq. 4.

$$s_1 - s_1^0 = s_2 - s_2^0 = s_3 - s_3^0$$

Since these three quantities are equal to each other, they all may be set equal to a fourth quantity, which is to be considered a variable, thus:

$$\begin{aligned} s_1 - s_1^0 &= b, s_2 - s_2^0 = b, \text{ and } s_3 - s_3^0 = b \\ \text{or} \\ s_1 &= s_1^0 + b, s_2 = s_2^0 + b, \text{ and } s_3 \\ &= s_3^0 + b \quad [7] \end{aligned}$$

In the theory of elasticity and plasticity, there is a quantity called the "stress

deviation," which is defined simply as the difference between the principal stress operating in one of the principal directions and the average of all three principal stresses. Thus the defining equations for the three stress deviations, S_1 , S_2 , and S_3 are:

$$\begin{aligned} S_1 &= s_1 - \left(\frac{s_1 + s_2 + s_3}{3} \right) \\ S_2 &= s_2 - \left(\frac{s_1 + s_2 + s_3}{3} \right) \\ S_3 &= s_3 - \left(\frac{s_1 + s_2 + s_3}{3} \right) \end{aligned} \quad [8]$$

The stress deviations for a stress system defined by any point lying on the meridian in question may be obtained by substituting the coordinates of any point on the meridian as given by the parametric Eqs. 7 in the defining Eqs. 8. For the case of S_1 we obtain:

$$\begin{aligned} S_1 &= s_1^0 + b \\ &\quad - \left(\frac{s_1^0 + b + s_2^0 + b + s_3^0 + b}{3} \right) \\ &= s_1^0 - \left(\frac{s_1^0 + s_2^0 + s_3^0}{3} \right) \end{aligned}$$

Substituting Eq. 6 in this expression reduces it to:

$$S_1 = s_1^0 = \text{constant} \quad [9]$$

It can be shown similarly that

$$\begin{aligned} S_2 &= s_2^0 = \text{constant and } S_3 = s_3^0 \\ &= \text{constant} \quad [9] \end{aligned}$$

Thus the meridians may be interpreted as the loci of points for which the three principal stress deviations are constant.

STRAIN RATES AND THE EQUATIONS OF CONSTANT VOLUME

The Huber-von Mises-Hencky cylinder describes a locus: it is an expression for all possible principal stresses that can exist if the metal is in a plastic state. The counterpart to it, which describes all possible principal strain rates that can exist if the metal is in a plastic state,

^{*} Because the meridian is defined by this point, we shall call the vector passing through this point and the origin of the coordinate system the "defining stress vector."

can be derived from the assumption that the volume of a metal being deformed remains constant (an assumption that is true to within 0.01 to 0.1 per cent). This assumption can be expressed mathematically by the following equation:

$$e_1 + e_2 + e_3 = 0 \quad [10]$$

where e_1 , e_2 , and e_3 are the principal strains.*

From Eq. 10 it follows that,

$$\frac{de_1}{dt} + \frac{de_2}{dt} + \frac{de_3}{dt} = 0 \quad [11]$$

If the quantities de_1/dt , de_2/dt , de_3/dt , are ascribed to the coordinate axes of a three-dimensional Cartesian system, this expression is the equation of a plane passing through the origin, whose normal is equally inclined to the three coordinate axes.

The strain rates that may exist at a point in the metal at any given instant of time will be expressed by some point in this geometric plane. A vector may be drawn through this point and the origin of the Cartesian system. In this case, the coordinates of the point de_1/dt , de_2/dt , and de_3/dt will become the components of the vector.

From this point on, we wish to consider the two three-dimensional Cartesian systems discussed so far as being coincident; i.e., the two origins shall be considered coincident, the s_1 , de_1/dt axis shall be considered coincident, the s_2 , de_2/dt axis shall be considered coincident, and so on.

ST. VENANT EQUATION

The St. Venant equation⁷⁻¹⁰ answers

* In this work, the strain e is defined by the equation:

$$e = \ln \frac{l}{l_0}$$

where l_0 and l are the lengths of an element before and after deformation, respectively. Mention might be made here, too, of the well-known fact that the directions along which the three principal strains lie are coincident with the directions in which the principal stresses operate.⁶

the question: What will be the relative rates of deformation of the metal under a particular stress system?

According to this equation, the strain rate in a particular principal direction will be directly proportional to the principal stress deviation in that direction, thus:

$$\begin{aligned} \frac{de_1}{dt} &= cS_1 \\ \frac{de_2}{dt} &= cS_2 \\ \frac{de_3}{dt} &= cS_3 \end{aligned} \quad [12]$$

where c is a constant. These equations are sometimes assembled into the ratio:

$$de_1:de_2:de_3::S_1:S_2:S_3 \quad [13]$$

Graphically interpreted, these equations show that any point on a single meridian will produce the same relative strain rates. Further, in view of Eqs. 9, Eq. 13 becomes:

$$de_1:de_2:de_3::s_1^0:s_2^0:s_3^0 \quad [14]$$

Thus we see that (with the two coincident Cartesian coordinate systems) the vector describing the relative strain rates coincides with the defining stress vector (see footnote on p. 3) that corresponds to the point describing the particular stress state giving rise to the strain rates.

Let us illustrate this important fact with a graphical example. Presume that the metal is subjected to the stress system defined by the point P in Fig. 2. This point lies on the meridian PP'' whose defining stress vector is OP' . The relative strain rates produced by the stress system P will be proportional to the components (in the direction of the coordinate axes) of the vector OP' .

This relationship points the way to an extremely rapid method of determining relative strain rates if the stress system is known or, conversely, of determining the relative values of the three principal stresses if the strain rates are known.

THE ISOMETRIC PLOT

We now propose to represent the two coincident three-dimensional Cartesian systems on an isometric plot. In this case,

To illustrate the use of the isometric plot in determining relative strain rates if the stress system is known, consider a simple tensile test. In this instance there

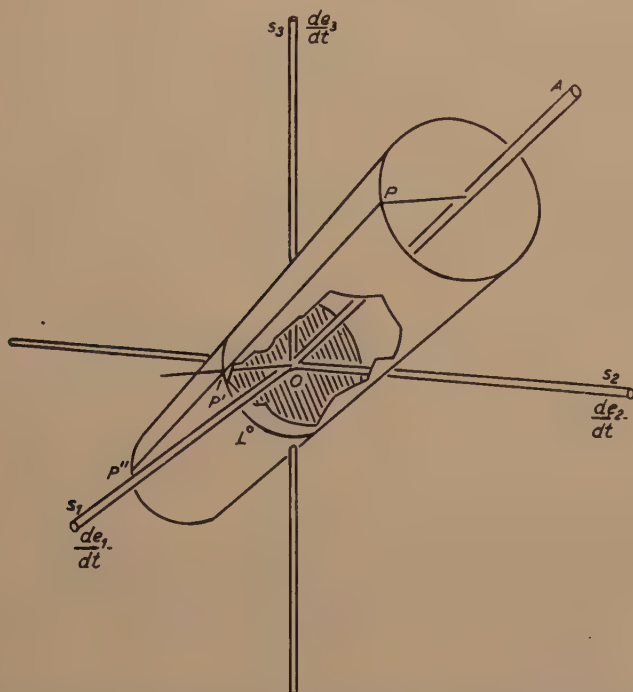


FIG. 2.—TWO COINCIDENT THREE-DIMENSIONAL CARTESIAN SYSTEMS.

The Huber-von Mises-Hencky cylinder is broken away to reveal the origin of the systems as well as the plane normal to the cylinder axis A passing through the origin. This plane is shaded in the drawing. The point P lies on the meridian PP'' , which intersects the circle of latitude L^0 at P' . The components (in the direction of the coordinate axes) of the vector OP' (lying in the shaded plane) are proportional to the relative strain rates de_1/dt , de_2/dt , and de_3/dt , produced by the stress system defined by the point P .

the cylinder shown in Fig. 1 appears as a circle,* the axis of symmetry as a point at the center of the circle, meridians appear as points on the circle, and the defining stress vector and the strain rate vector appear as some line lying in the plane of the paper or drawing and passing through the center of the circle (Fig. 3).

* This proposed method of representation can be employed to advantage to plot stress data testing the validity of the Huber-von Mises-Hencky equation, especially for cases where the data do not describe a condition of plane stress (i.e., for cases where one of the three principal stresses is not zero).

are no shear stresses operating on the cross-sectional plane of the tensile specimen or any plane perpendicular to this plane. The three principal directions are, therefore, the longitudinal axis of the specimen and any two transverse axes that are perpendicular to each other. In the first principal direction, the principal operating stress is, of course, the tensile stress that exists at the particular moment in question in the tensile test, whereas there are no stresses in the other two principal directions. Thus $\sigma_1 = K$, $\sigma_2 = 0$, and $\sigma_3 = 0$.

or $s_1 = 1$, $s_2 = 0$, and $s_3 = 0$. Turning to Fig. 3, we lay off the point P one unit in the s_1 direction and zero units in the s_2 and s_3 directions. The strain-rate sector

in Fig. 2. This determination can, however, be carried out more simply on the isometric plot itself.

In Fig. 4, the isometric plane passing

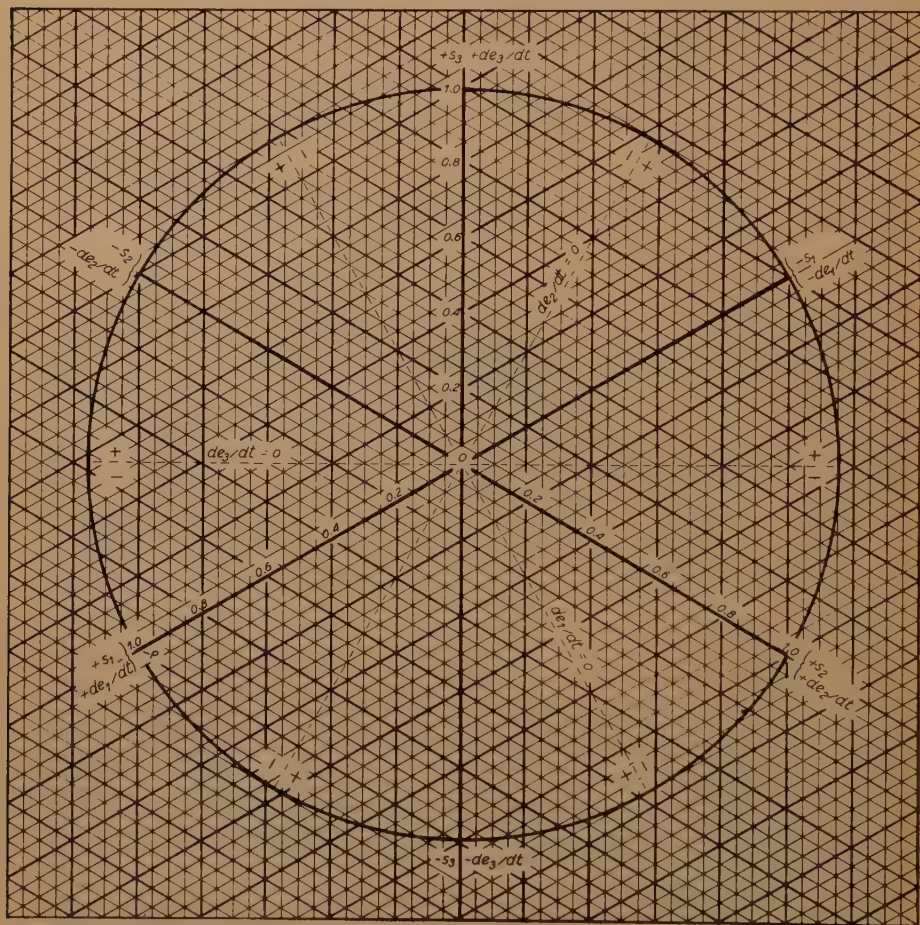


FIG. 3.—ISOMETRIC PLOT OF HUBER-VON MISES-HENCKY AND ST. VENANT RELATIONS.

The Huber-von Mises-Hencky cylinder shown in perspective in Fig. 1 appears now as if viewed from a point on the cylinder axis A of that illustration, all foreshortening being disregarded. The cylinder itself appears as a circle, the cylinder axis A , as well as the origin of the three-dimensional system (Fig. 2), appears as a point at the center of the circle. The meridians M shown in Fig. 1 appear as points on the circle. The defining-stress vector and the strain-rate vector appear as straight lines in the plane of the drawing passing through the center of circle.

will pass from the center of the circle through the point P . All that is required to determine the relative strain rates is to read off the projection of the vector OP on the three coordinate axes as was shown

through the origin of the three-dimensional system is indicated together with the vector OP , the projection of the latter on the s_3 , de_3/dt axis as well as a line lying in the isometric plane for which

$de_3/dt = 0$. The distance D_3 between this latter line and the point P taken perpendicularly to the line $de_3/dt = 0$ (or, relatedly, parallel to the plane passing

isometric plane from the point P to the three lines $de_1/dt = 0$, $de_2/dt = 0$, and $de_3/dt = 0$.

To return to Fig. 3, the point P lies

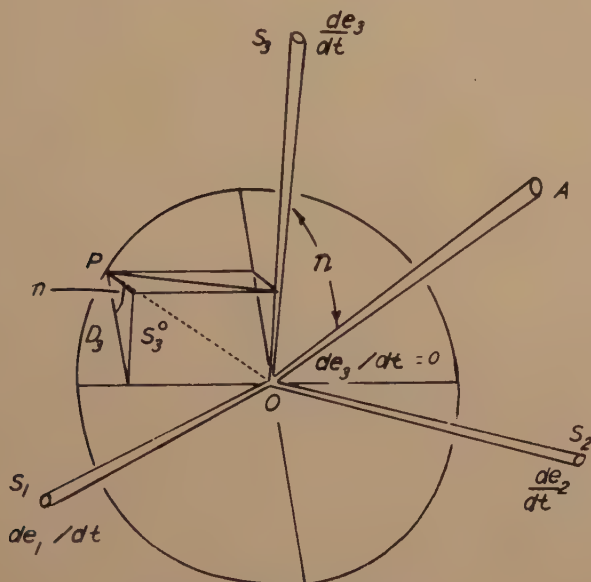


FIG. 4.—RELATIVE STRAIN RATES.

The isometric plane is shown passing through the origin O of the system perpendicular to the axis A . The vector OP lies in the isometric plane, as does a line $de_3/dt = 0$. The component of OP lying in the s_3 direction is labeled s_3^0 . The distance from P to the line $de_3/dt = 0$ is labeled D_3 . The line D_3 is parallel to a plane passing through the s_3 , d_3/dt axis and A . The axis A forms the angle n with the s_3 , d_3/dt axis.

through the axis A and the s_3 , de_3/dt axis) may be expressed as function of the component s_3^0 in the following manner:

$$D_3 = \frac{s_3^0}{\sin n}$$

It can be shown by similar means that:

$$D_1 = \frac{s_1^0}{\sin l} \text{ and } D_2 = \frac{s_2^0}{\sin m}$$

Since $l = m = n$, we may write:

$$de_1:de_2:de_3::s_1^0:s_2^0:s_3^0::D_1:D_2:D_3$$

Thus in the isometric projection, the relative strain rates can be determined by measuring each of the distances on the

one unit* from the line $de_1/dt = 0$, and -0.5 units from the lines $de_2/dt = 0$ and $de_3/dt = 0$, thus indicating that:

$$de_1:de_2:de_3::2:-1:-1.$$

i.e., the specimen will elongate in the direction of the longitudinal axis at a rate twice as great as that at which it contracts in any transverse direction. This relationship is commonly known to exist for the case of simple tension, and may be checked arithmetically by Eqs. 8 and 13.

* While the scales in Fig. 3 represent distances along the three stress or strain-rate axes, there is no reason why they cannot be used to measure distances in the plane of the paper itself.

The converse problem of determining relative stresses, being given the relative strain rates, is made simpler by the fact that:

$$\frac{de_1}{dt} + \frac{de_2}{dt} + \frac{de_3}{dt} = 0 \quad [11]$$

by Eq. 11. The point at which the vector OP' intersects the plasticity circle will give the relative stresses corresponding to the deformation.

SUMMARY

A method of representing the Huber-

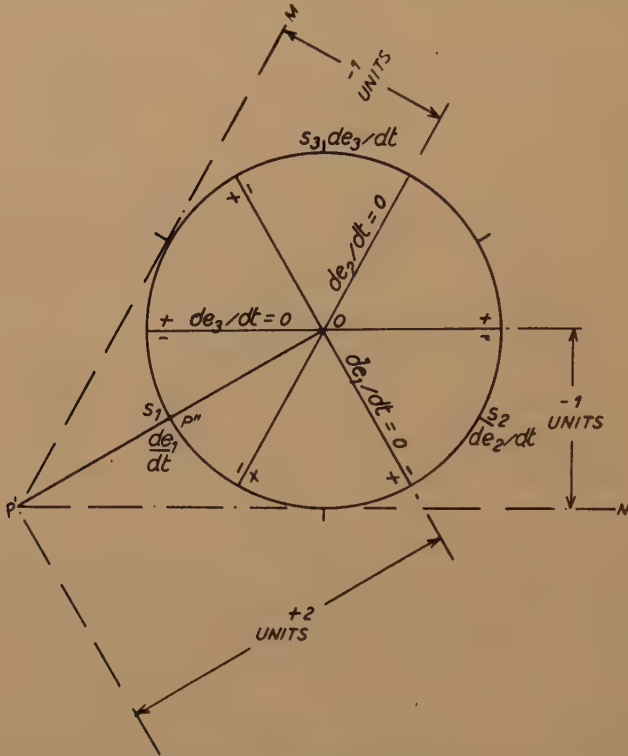


FIG. 5.—RELATIVE STRESS RATE.

The relative strain rate $de_2/de_3 = -1/-1$ is given. Line MP' is laid off -1 units from the line, $de_2/dt = 0$; line NP' is laid off -1 units from the line, $de_3/dt = 0$. A vector is drawn from the origin O through the intersection of lines MP' and NP' . This vector intersects the plasticity circle at a point P' .

Hence, if any two of the three terms are known, the third is determined. Presume, for example, that the ratio $de_2/de_3 = -1/-1$ is known. A line -1 units from the line $de_2/dt = 0$ is laid off (Fig. 5), and another -1 units from the line $de_3/dt = 0$ is drawn in. The intersection of these two lines determines a vector OP' . P' lies 2 units from the line $de_1/dt = 0$ as demanded

von Mises-Hencky equation as a circle on an isometric plot is proposed.

A rapid graphical method employing the proposed isometric plot for determining relative strain rates knowing the stresses existing in a metal in the plastic state (or conversely, of determining the relative stresses knowing the strain rates) is described. Simple examples are given.

ADDENDUM

It was mentioned in the footnote on page 5 that the isometric plot would be a convenient method of plotting data that have been procured to test the validity of

Further, Eq. 6 should be recalled:

$$s_1^0 + s_2^0 + s_3^0 = 0 \quad [6]$$

If this equation is to have a nontrivial solution, there must be at least one positive

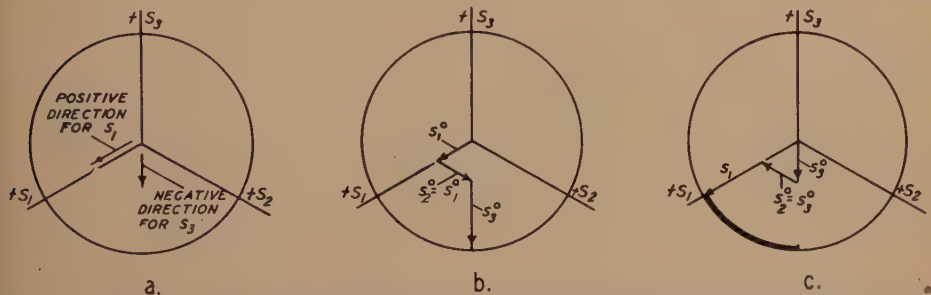


FIG. 6.—DATA OF HUBER-VON MISES-HENCKY EQUATION PLOTTED ON PART OF ISOMETRIC PLOT.
 a. Isometric plot of plasticity circle showing directions in which quantities s_1^0 and s_3^0 are plotted if Eq. 15 is followed.

b. Isometric plot showing one limit of plasticity circle that is used for the case where s_2^0 assumes its largest possible value provided Eq. 15 is satisfied.

c. Same as Fig. 6b for case where s_2^0 assumes its smallest possible value as defined by Eq. 15.

the Huber-von Mises-Hencky equation. It may be mentioned here that these data may be plotted in a very abbreviated part of the isometric plot. This is analogous to the way in which crystallographic data can be plotted on a "stereographic triangle" that composes only one-twenty-fourth of the crystallographer's Wulff net. This convenience is possible if (as is usually done in plasticity work) the quantities s_1 , s_2 , and s_3 are assigned to the three principal stresses so that s_1 corresponds to the algebraically largest stress, s_2 to the next largest, and s_3 to the algebraically smallest stress; i.e.,

$$s_1 \geq s_2 \geq s_3$$

In the light of Eq. 7, this expression transforms to

$$(s_1^0 + b) \geq (s_2^0 + b) \geq (s_3^0 + b)$$

Subtracting the quantity b from each term leads to

$$s_1^0 \geq s_2^0 \geq s_3^0 \quad [15]$$

quantity and one negative quantity, and in view of expression 15, s_1^0 will be the positive term while s_3^0 will be the negative one. Further, from Eq. 15, we see that the algebraically largest value that s_2^0 can assume is $s_2^0 = s_1^0$ while the algebraically smallest value that s_2^0 can assume is $s_2^0 = s_3^0$.

On the isometric plot then, s_1^0 can be laid off only in the positive direction while s_3^0 can be laid off only in the negative direction as indicated by the arrows in Fig. 6a. The case where $s_2^0 = s_1^0$ is treated in Fig. 6b. Three arrows indicate the values of s_1^0 , s_2^0 and s_3^0 and the resultant point falls at a "six o'clock" position on the circle. The case where $s_2^0 = s_3^0$ is illustrated in Fig. 6c. Here the three arrows indicating the values of s_1^0 , s_2^0 and s_3^0 lead to a point on the circle at an "eight o'clock" position. It can be shown that any intermediate value of s_2^0 would yield a point on the circle somewhere between these two limits (as indicated by the heavy line in Fig. 6c). Hence, if the con-

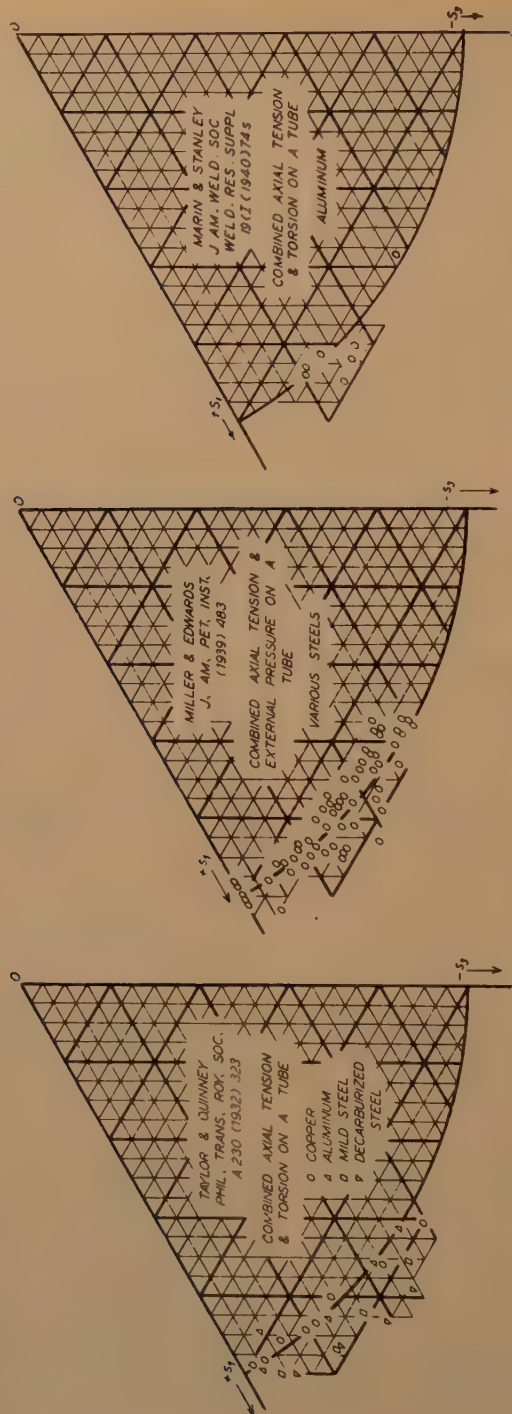


FIG. 7.—DATA TESTING VALIDITY OF HUBER-VON MISES-HENCKY EQUATION PLOTTED ISOMETRICALLY.
Data taken from (a) Taylor and Quinney,⁸ (b) Miller and Edwards,¹¹ and (c) Marin and Stanley.¹²

vention given in Eq. 15 is adhered to all stress data can be recorded on a sextant of the plasticity circle whose limits are the intersections of the $+s_1$ and $-s_3$ axes with circle itself. Some recent data published by Taylor and Quinney,⁶ Miller and Edwards,¹¹ and Marin and Stanley,¹² testing the validity of the Huber-von Mises-Hencky equation, is recorded in this manner by way of illustration in Fig. 7.*

ACKNOWLEDGMENT

It is a pleasure to acknowledge the encouragement and advice of Dr. H. P. Croft, Director of Research and Technical Control, Midwestern Division, Chase Brass and Copper Company, Inc., Euclid, Ohio, in this work.

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6. Taylor and Quinney: *Phil. Trans., Roy. Soc.* (1932) A-230, 323.
7. St. Venant: *Compt. rend., Acad. Sci. Paris*, (1870) 70, 473.
8. Levy: *Compt. rend., Acad. Sci. Paris* (1870) 70, 1323.

* Not all of Miller and Edwards' data have been included here. Their experimental work was conducted, as indicated in Fig. 7b on tubes under axial tension and external pressure. The tubes would yield in either one of two ways: either in tension in the direction of the axis of the tube or by collapsing. While the plastic collapse data fall along the plasticity circle, these data should be regarded as proof of certain collapse behavior with which their paper deals and not as proof of the Huber-von Mises-Hencky equation. Further, no data for yielding along the axis of the tube have been included for the cases where external pressure led to a hoop stress that was numerically greater than the axial tensile stress, since by the St. Venant principle, yielding would have occurred to a greater extent in circumferential direction of the tube (in which direction no strain measurements were made) than in the direction of the axis of the tube (in which direction, strain measurements were made). The determination of the yield point in these cases may possibly have been affected to a slight extent by this fact.

9. Roß and Eichinger: Report No. 28, Eidgenössische Materialprüfungsanstalt, Zürich, 1926.
10. Lode: *Ber. Werkstoffausschuss, V.D.E., Düsseldorf* (1925).
11. Miller and Edwards: *Jnl. Amer. Petr. Inst.* (1939) 483.
12. Marin and Stanley: *Jnl. Amer. Weld. Soc., Weld. Res. Suppl.* 19 (1940) 1, 748.

DISCUSSION

M. G. CORSON.*—I believe there is a definite danger in the metallurgical circles of substituting purely mathematical imagery, whose production costs are infinitesimal, for technically feasible but financially almost impossible experimentation. So Dr. Baldwin begins by giving an equation tentatively developed by Von Mises in 1913 and containing three principal stresses, none of which can be experimentally determined, instead of formulating it in plain words: A plastic deformation starts when the stress acting in its direction surpasses the yield point by the latter's own value, assuming that the two perpendicular stresses cannot hamper its action by stresses more than half that value.

The approach to the strain-rate question begins with a faulty assumption that the volume of the metal being deformed remains constant. This is not true either for the purely elastic range or for the finished state, because the densities of a cold-rolled or cold-drawn metal are always lower than those of a properly made and annealed metal. The deviations of density reach from 0.5 to 2 per cent. I do not know what the density of a metal in the process of plastic deformation might be (does the author know it?) but it is hardly any higher than in the state-past deformation. So his assumption is not true within 0.01 to 0.1 per cent as he states. Therefore, Eq. 10 being faulty, the Eq. 11 becomes faulty too.

I do not see why a strain should be defined by the formula $e \ln \frac{l}{l_0}$. In fact, even if there were a good theoretical reason for this it would have no practical meaning because in the case of the very small local strains the $\ln \frac{l}{l_0}$ equals $\frac{l-l_0}{l_0}$ with a precision far higher than any experimental determination of the deformation could yield.

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St. Venant's equation 12 is logical if we grant all his assumptions—the assumptions of a pure mathematician working in 1870 when a metal was only a continuum with the hypothetical atoms forming knots in that continuum—if that much. His assumption that the rates of strain development are proportional to the stresses has no basis in fact.

The statement on page 61 that a specimen will elongate along the longitudinal axis at a rate twice as high as it will contract in any transverse direction is a mere repetition of that assumption whose faultiness was indicated in my paragraph 2. This last statement is faulty for both the elastic and the plastic deformation. For elastic deformation it contradicts the values of the elastic ratios, wrongly called Poisson's ratios. For a deformation during the plastic process the statement is simply devoid of foundation.

I do not belong with those who hate the mathematical method. Nothing is pleasanter than to follow a mathematical development solidly rooted in the results of a precise experimentation. But the mathematics offered in Dr. Baldwin's paper does not appear to me to be meaningful. I wonder very much if it ever might help to turn out a better wire or strip of any metal.

W. M. BALDWIN (author's reply).—Mr. Corson has raised several points; with regard to most of them, it is perhaps best to refer him to a number of standard treatises and textbooks where he can find the fuller explanation he requires, and which, because of limitations of space, it would be impossible to give here.

General experimental methods of determining the three principal stresses are given in such texts as those by Nadai,¹³ Love,¹⁴ Southwell.¹⁵ Specific reports on experiments in which the three principal stresses are determined (both as to direction and magnitude) would include references 9 through 12 of the paper as well as Hohenemser's¹⁶ excellent report.

The reasons for defining strain as $\ln l/l_0$ and

its practical meaning when so defined are explained in Ludwik,¹⁷ Sachs,¹⁸ and Gensamer.¹⁹

Mr. Corson is quite correct in attacking the author's statement that the assumption that a metal is constant in volume is correct to within 0.01 to 0.1 per cent. A better statement would have been that the assumption is true to within a very low percentage depending upon the metal and type of deformation. For copper, the value would appear to be of the following magnitude: 0.12 per cent for rolling,^{20,21} 0.13 per cent for uniaxial stretching,²² 0.25 per cent for drawing, twisting, or spiral rolling;²⁰ for other metals, the variation in specific volume is less systematically reported, but it appears that Mr. Corson's value of 2 per cent would be in order for some cases. This change is a minor one, however, and by no means justifies Mr. Corson's statement that the conclusions reached regarding the relative strain rates involved in a tensile test are "simply devoid of foundation." From Maier's data for iron,²⁰ it would appear that at the deformations at which 1 per cent deviation from the starting volume occurs, a hypothetical tensile-test specimen would display strain rates of 2.00759, -1 , -1 instead of 2, -1 , -1 .

The St. Venant relations have been experimentally investigated and experimental results have been compared with theory (references 6, 9 and 10). This is actually the roughest approximation contained in the paper, but one that is accepted by workers in the field of plasticity.

The practical use of the mathematics and the application of this work to "turn out a better . . . strip of any metal" are indicated in the author's discussion on page 67.

J. MARIN.*—The author of this paper has presented an interesting and useful graphical representation of the distortion energy theory, or the Huber-Von Mises-Hencky theory. It should be noted, however, that the dis-

¹⁷ Ludwik: *Elemente der technologischen Mechanik*. Berlin 1909. J. Springer.

¹⁸ Sachs: *Spanlose Formung*. Berlin 1930. J. Springer.

¹⁹ Gensamer: *Strength of Metals*. Education Lectures, Amer. Soc. for Metals, 1940.

²⁰ Maier: *Trans. A.I.M.E.* (1936) **122**, 121.

²¹ Wood: *Phil. Mag.* (1934) **18**, 495.

²² Ueda: *Sci. Repts. Tohoku Imp. Univ.* (1930) [1] **19**, 473.

* Professor of Engineering Mechanics, Pennsylvania State College, State College, Pennsylvania.

¹³ Nadai: *Plasticity*. New York, 1931. McGraw-Hill Book Co.

¹⁴ Love: *Mathematical Theory of Elasticity*. Cambridge University Press.

¹⁵ Southwell: *Theory of Elasticity*. Oxford University Press, 1936.

¹⁶ Hohenemser: *Ztsch. angew. Math. und Mech.* (1931) **11**, 15.

tortion-energy theory as given by Eq. 1 does not give the relations between the principal stresses in the plastic range but gives the relation between these stresses when yielding or plastic flow begins. In some experimental studies on combined stresses the beginning of yielding has not been accurately defined and correlated with the beginning of yielding under simple tension; that is, the method of defining yielding in simple tension should be related in some rational way to the method used to define yielding in the case of combined stress. If the offset yield strength is used for defining the yield stress K in simple tension, an equivalent offset strain value for defining the yield stress in combined stresses may be obtained¹ and a consistent procedure for both simple tension and combined stresses is thereby used.

For ductile materials a consideration of distortion energy appears to be basic in not only defining the beginning of static yield

under combined stresses (as discussed in the author's paper), but also to predict fatigue strength under combined stresses.² The creep strains in materials subjected to combined stresses accompanied by creep have also been approximately determined on the basis of a distortion-energy criterion.³ More recently a distortion-energy criterion has been used to predict plastic strain under combined stresses. It may be of interest to apply the author's graphical method to the foregoing conditions of fatigue, creep and plastic flow.

W. M. BALDWIN, JR.—Professor Marin's remarks are welcome. They focus attention on the practical execution of the work treated mathematically in the paper. His suggestions with regard to the application of the method to conditions of fatigue, creep and plastic flow are a partial answer to Mr. Corson's question as to the meaning or use of the paper.

²⁴ J. Marin: Working Stresses for Members Subjected to Fluctuating Loads *Trans. A.S.M.E.*, **59**, A-55.

²⁵ C. R. Soderberg: The Interpretation of Creep Data in Engineering Design. *Trans. A.S.M.E.*, Nov. 1936, p. 733.

²³ J. Marin: A Method of Defining Failure in Members Subjected to Combined Stresses *Trans. Amer. Soc. for Metals*, Dec. 1941, p. 1013.

Young's Modulus—Its Metallurgical Aspects

BY DAVID J. MACK,* MEMBER A.I.M.E.

(New York Meeting, October 1945)

A SURVEY and critical appraisal of published information about Young's modulus was originally made by the writer because of a complete lack of information about this very important quantity in works on mechanics, physical metallurgy, physics, and other sciences. It was felt that a comprehensive summary of such information about Young's modulus might be of general interest and may suggest new problems or lines of attack on other problems that involve E . Hence this paper has been prepared even though it is only a review, with no new ideas or experimental data. The references are only those used in assembling the paper. No attempt was made to compile a complete bibliography on the subject of Young's modulus.

CALCULATION OF YOUNG'S MODULUS FROM THEORETICAL OR EMPIRICAL CONSIDERATIONS

Many attempts have been made to compute E from theoretical considerations. The earliest calculations were probably those of Tomlinson (1883) and Southerland (1891), but Fessenden^{41,42} made extensive calculations a few years later and arrived at the relationship:

$$E = 78 \cdot 10^{12} \left(\frac{1}{V} \right)^{\frac{1}{3}}$$

where V is the atomic volume. In 1923,

Manuscript received at the office of the Institute April 18, 1945; revised June 8, 1945. Issued as T.P. 1936 in METALS TECHNOLOGY, December 1945.

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⁴¹ References are at the end of the paper.

Peczalski,⁴³ working from the same standpoint but with more information available on atomic structure, arrived at an identical relationship, which he expressed as:

$$E = B \left(\frac{\rho}{m} \right)^2$$

where B is a constant of value about $8 \cdot 10^7$, ρ is density and m is atomic weight; the atomic volume, of course, being m/ρ . Portevin⁴⁴ immediately pointed out that while the equations of Fessenden and Pecalski were true of the common metals, they gave low values for the refractory metals with high moduli (Fig. 1). He showed (Fig. 2) that much better concordance was obtained by means of an empirical equation of the form:

$$E = \frac{KT^a}{V^b}$$

where K is a constant; T the absolute melting point; V , atomic volume, and a and b constants of value approximately 1 and 2 respectively. This constant K in the Portevin equation is not necessarily the same for all elements, as shown by Thompson.⁴⁵ Other equations for E based upon theoretical considerations have been derived by Honda and Yamada⁴⁶ and Lasareff.⁶⁰

The most recent calculations of elastic moduli based upon quantum mechanics are probably those of Fuchs.⁴⁶⁻⁴⁸ He extended the method of Wigner and Seitz for calculating the lattice energy and compressibility of monovalent metals and computed the elastic constants of lithium,

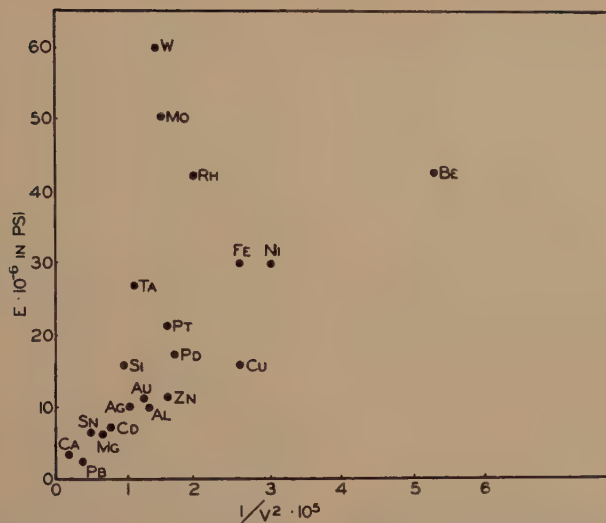


FIG. 1.—YOUNG'S MODULUS AS A FUNCTION OF ATOMIC VOLUME, PLOTTED FROM THE PECZALSKI

$$\text{EQUATION } E = B \left(\frac{\rho}{m} \right)^2.$$

Data from Metals Handbook, 1939 Edition.

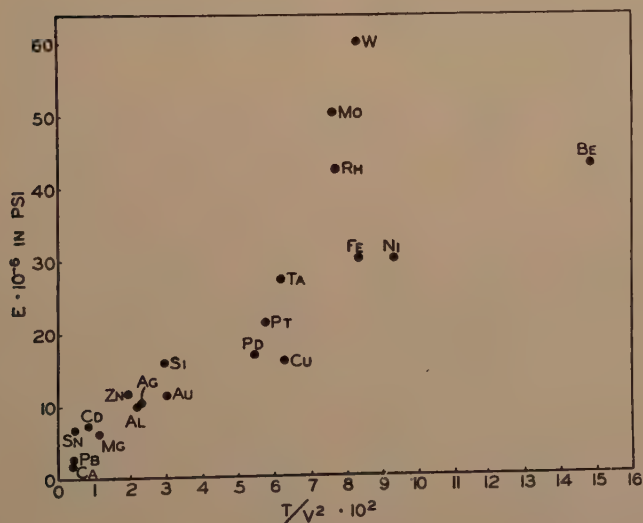


FIG. 2.—YOUNG'S MODULUS AS A FUNCTION OF T/V^2 PLOTTED FROM PORTEVIN'S MODIFICATION OF THE FESSENDEN-PECZALSKI EQUATION $E = KT/V^2$.
Data from Metals Handbook, 1939 Edition.

sodium, potassium and copper. Agreement was good with experimental values.

A number of empirical relations have been derived between the elastic coefficients, notably the modulus of compressibility or its inverse, with such quantities as surface tension, coefficient of cubical expansion, specific heat, etc.,^{44,51} but all are similar to Portevin's equation. Andrews⁵² has reexamined the entire problem of the correlation of Young's modulus with other physical quantities and concludes that the best correlation is given by the equation:

$$E = \frac{bA}{V^x} \frac{C e^T}{V^x}$$

where C , b , and x are constants, V is atomic volume, A is absolute temperature and T the melting point. This equation is similar to Portevin's but takes into account the temperature as suggested by Guillet.¹⁰

EXPERIMENTAL DETERMINATION OF YOUNG'S MODULUS

Many methods have been used to determine Young's modulus experimentally. All of these fall into either one of two categories: static or dynamic. The commonest methods of each class will be described.

Static Methods

The oldest of these methods, and still the most widely used, is the stress-strain method, the modulus being the slope of the straight-line portion of the stress-strain curve lying below the proportional limit. Experimentally it is only necessary to conduct a tensile (or compressive) test of the material in question and construct the stress-strain curve from which the modulus may be read directly. The plotting of stress-strain curves is not a difficult matter, and is unnecessary if a testing machine is equipped with an autographic stress-strain recorder. Guillet^{1,2} has described the various aspects of this method

in considerable detail. It may be termed the "standard" method if such a thing exists, because it is a direct method and does not involve controversial mathematical considerations. The only assumption made is that the load is uniformly distributed over the entire cross section, which is essentially realized if the longitudinal dimensions of the specimen are sufficiently large in relation to the transverse dimensions. The cross-sectional shape of the specimen is immaterial as long as it is uniform.

The principal difficulty consists in loading the specimen in "pure" tension; that is, in obtaining an elongation that is identical for all sections of the specimen. Another difficulty is the necessity of maintaining the specimen at constant temperature during an entire run, otherwise the thermal dilation is algebraically added to the elastic deformation, vitiating the results. Guillet¹ shows that a variation in temperature of 5° may cause an error of 5 per cent in the modulus. Isothermal conditions are maintained during a run by enclosing the specimen in a box.* This tensile method is not readily adaptable to brittle or friable material such as glass, silica, bismuth wire, etc., or to very soft materials such as lead. Nor is it useful for very small specimens or samples.

The most widely used indirect static method for the determination of Young's modulus is by studying the flexure (bending) of simple beams and constructing the load-deflection curve. This method has been described by Benedicks,³ Guillaume,⁹ Nishiyama,⁷ Ichinose,⁸ Shakespear,⁴ Weston,⁵ Guillet,^{1,10} and others. It has the advantage of giving the deformation very sensitively with load, the deformation usually being measured by an optical lever system^{7,8,9} or even by means of an

* The example used by Guillet is the draft from an open window blowing on the specimen. Probably more commonplace is a too rapid pulling rate, which causes a rise in temperature of the specimen.

interferometer.^{4,5} The chief objections to this method are: the inequality of the moduli in tension and compression, the displacement of the neutral axis of the beam during loading, and whether the modulus is the same for all sections of the beam between the neutral "fibers" and those most highly stressed. These objections have led several writers^{1,11} to describe the method as one of "heterogeneous" deformation and hence not suitable for the determination of Young's modulus. Lea, Collins and Reeve⁶⁶ have shown that for thin-walled tubes the modulus determined by flexure is generally about 7 to 10 per cent greater than the modulus determined by the tensile method. The limits within which the method of flexure is applicable have been analyzed mathematically by Hummel and Morton.¹³

A similar method employing a column instead of a beam has been used by Meisser.¹² He found that if the longitudinal load on a thin rod is increased a little beyond the critical value, the rod will deflect sideways by an amount that depends very sensitively on the load and the elastic constants of the material. Experimentally, Meisser's method is more difficult to use than the beam method and is subject to even greater theoretical troubles.

The elastic deflection of helical springs has also been used^{14,15} to determine the elastic modulus, particularly in studying the effect of hydrostatic pressure. However, it is the modulus of rigidity (shear) that is determined in this case. The experimental and theoretical difficulties are the same as in the deflection of beams. Other static methods for the determination of Young's modulus have been used^{18,19} and proposed but they are all closely related to the methods just described.

Dynamic Methods

All the dynamic methods of determining Young's modulus are based upon the fact

that the elastic constants of a material largely determine its vibratory characteristics. Because of this fact, this field has largely been explored by the physicists.

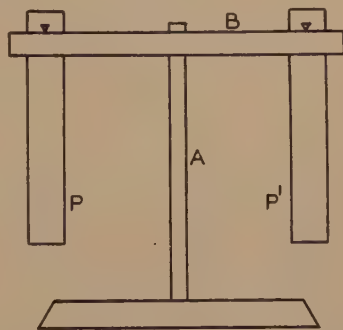


FIG. 3.—TWIN PENDULUMS OF LE ROLLAND AND SORIN.

A, specimen; *B*, rigid bar; *P* and *P'*, identical pendulums resting on knife edges on *B*.

Of the many dynamic methods available, one of the best, and certainly the simplest, is the twin pendulum method of LeRolland and Sorin,¹⁷ which has been extensively analyzed mathematically by Guillet.² The specimen *A* (Fig. 3) made of the material to be studied is rigidly fixed at its lower end and is fitted at the upper end with a rigid bar *B*. *P* and *P'* are two identical pendulums resting on *B*. With *P* at rest, one swings *P'* with any amplitude desired. *P* will then be set in motion under the influence of the small displacement impressed on the specimen by *P'*. *P'* decreases in amplitude and transmits its energy to *P*. *P'* finally comes to rest and *P* oscillates with maximum amplitude. The process then reverses itself. If κ is the time that separates two arrests of one of the pendulums, then Young's modulus, E , is equal to κA where A is a constant, determined on a substance whose modulus is known. This method realizes the optimum conditions of small elastic strain and no confinement of the material. The values obtained check very closely those obtained by direct measurement from the stress-strain curve as shown in Table 1.

TABLE I.—*Comparison of Values of Young's Modulus Obtained by Different Methods*¹⁰

Material	<i>E</i> from Stress-strain Curve, Lb. per Sq. In.	<i>E</i> from Twin Pendulums, Lb. per Sq. In.
Copper.....	18,480,000	18,480,000
Bronze E2.....	17,910,000	18,050,000
Bronze E6.....	17,010,000	17,070,000
Bronze E10.....	16,020,000	15,630,000

Haupt²⁰ also gives comparative values of *E* determined by different methods and points out some of the reasons for lack of agreement in some of the figures he cites (also see Ide²⁵). There is reason to believe, however, that values of *E* determined by static methods should not necessarily agree with values obtained by dynamic methods as pointed out by Ichinose³ and Thompson.²¹ Static methods give an isothermal modulus while dynamic methods may give an adiabatic modulus,* the difference between the two sometimes being as great as 20 per cent, the adiabatic modulus always being the greater.

Many of the dynamic methods depend upon the vibratory characteristics of the material differing from one another chiefly in the method of inducing the specimen to vibrate. This has been done by sonic and supersonic methods;^{21,22,24,27,31} by a piezoelectric oscillator;^{23,30} by electrostatic traction;^{20,25,31} by the use of a Stalloy armature attached to the free end of a cantilever beam;²⁶ by the determination of resonant frequencies in circular wire loops with a beat-frequency oscillator;²⁸ by using the mechanism of an electric clock to induce vibrations in a loaded spring²⁹ and others, including magnetic methods. Even the velocity of sound in the material has been used^{22,33} to determine Young's modulus. All of these methods are open to the same ob-

jection; i.e., they necessitate considerable mathematical treatment and complex apparatus. While they give valuable information about the elastic constants, many of them are more useful in the study of oscillation formulas. Their one great advantage over static methods is that they can be applied to very brittle materials.³⁹ Small specimens can also be used.

Certainly the most widely used dynamic method for the determination of the elastic constants is the torsion pendulum or torsion balance. Since this method gives the modulus of shear and not Young's modulus, only a few representative references are given.^{34,35,36} It is interesting to note that Jacquerod and Mügeli³⁶ combined the dynamic and static methods, enabling them to determine the shear modulus by either method. This was done by noting the time of swing of a torsion pendulum to which helical springs were attached. Torsional methods, like beam deflections, are based upon "heterogeneous" deformations¹ and hence are open to objection from a theoretical standpoint.

FACTORS AFFECTING MAGNITUDE OF YOUNG'S MODULUS

Crystallographic Effects, Anisotropy

Single crystals are generally anisotropic and the formulas relating stress to strain must take into account the variations in "stiffness" of the crystal in different directions. The result is that an elastic coefficient such as Young's modulus will have different values, depending upon the crystallographic direction in which it is measured. This fact has long been recognized by all workers in the field of plasticity. As shown by Barrett,⁶³ the maximum and minimum values of the tensile modulus and the compressive modulus vary widely in different metals. Tungsten is seemingly isotropic, with the same values in all directions; aluminum

* An illustration used by Ichinose is in the comparison of moduli determined from beam deflection where the same deflection is caused by a static load and a vibratory load.

varies only slightly, 1.21 to 1, while the ratio of maximum to minimum E in copper is 2.85 to 1; for zinc it is 3.55 to 1, and for beta brass it is 8.2 to 1.⁹³ These ratios are somewhat less than those quoted by Sayre.¹⁶

This effect of elastic anisotropy is most pronounced in single crystals, and should decrease as the number of crystals in the specimen increases (grain size decreases), provided the grains are oriented statistically at random, thus approaching elastic isotropy. Sayre¹⁶ shows that Young's modulus in a single crystal of iron may have values ranging from 19,000,000 to 41,000,000 lb. per sq. in., depending upon the crystallographic orientation, while the value of E commonly reported for polycrystalline iron is 29,500,000 lb. per sq. in. Boas⁵⁵ has computed the magnitude of this effect for tin by summation of the average values for single crystals over the whole range of orientation. Conversely, this can mean that as the grain size increases the elastic modulus of the material is apt to have different values in different directions, and this may lead to forming difficulties because of its effect on the plastic behavior of adjacent grains.* An extremely interesting discussion of this possibility is given by Sayre.¹⁶ On the other hand, a metal like aluminum, whose crystals show only slight elastic anisotropy, would not be expected to show a variation of Young's modulus with grain size. That this is true has been demonstrated by Sugihara,^{24,54} who found that wide variations in grain size in an aluminum rod did not appreciably affect E but did affect the elastic limit. Similar results were obtained by Köster⁵⁸ on aluminum of high purity and commercial purity, having a grain size range of 7.0 to 0.07 mm., a variation of one hundred fold in grain size.

* This is not to be confused with fibering, preferred orientation or texture in wrought polycrystalline material that results from other causes. Fibering will be discussed in the next section.

Preferred Orientation, Fibering, Deformation Textures

Because of the manner in which metal crystals deform plastically, cold-work tends to develop a type of preferred crystallographic orientation that corresponds with more favorable stress-distribution relationships than does random crystal orientation. The degree of this deformation texture depends on the metal, the manner in which it is worked and the degree of cold-working. Such a texture may or may not be removed by recrystallization. A great deal of attention has been given the subject because of its relation to the properties of commercial products. Barrett⁵³ devotes three chapters to it in his recent book on *The Structure of Metals*.

The development of such a preferred orientation is important because it gives rise to pronounced elastic anisotropy with resultant variations in Young's modulus in different directions in the sheet, rod, wire, tube, and other forms, even though the grain size is small. Bruggeman⁵⁶ has developed a theory for calculating the elastic moduli of crystals of regular metals of various textures; e.g., isotropic, cast, recrystallized, electrolytically deposited, rolled, drawn and beaten. He has also examined the part played by texture and other characteristics of polycrystalline metals in determining their elastic constants. Generally, Bruggeman found that texture played a predominant part, except in tungsten.

Working, Annealing and Recrystallization

Strangely enough, comparatively little was found in the literature on the effects of working on Young's modulus. Swift,⁵⁹ from an investigation of elastic strain, came to the conclusion that elasticity is a definite inherent property of materials, which is not destroyed by mechanical treatment and overstrain, and hence the modulus of a material should remain

practically unaffected by the elastic history and condition of the material. This belief was,⁶⁷ and still is, widely held, although it is unsupported by experimental evidence, as numerous investigators had shown,^{35, 73} even before Swift's paper appeared.

Honda and Yamada⁴⁹ found that Young's modulus decreases during cold-working in iron, steel, copper, aluminum and brass; the magnitude of decrease being about 3 per cent for single crystals of iron and 6 to 10 per cent for polycrystalline metals. They accounted for this decrease on the basis of theory. Kawai⁶⁰ found that for iron and steel the modulus was decreased by cold-working, first rapidly and then slowly. With copper, aluminum and nickel, the modulus decreased to a minimum and later increased with progressive cold-working. He also investigated the recovery of Young's modulus during annealing. With cold-worked iron and steel, the modulus increased rapidly at first and then more slowly as the annealing temperature rose to about 450°C., where recrystallization became noticeable. Above 450°C. the modulus continued to increase until at 900°C. it reached the original value it had before cold-working. With the copper, aluminum and nickel, the modulus reached its maximum value at 300°, 200° and 350°C., respectively (their approximate recrystallization temperatures), and then decreased until its original value was reached at about 650°, 500° and 900°C. Kawai attributed these changes to the combined effect of two opposing factors: the internal stresses caused by cold-working decreasing the modulus, and the appearance of texture, which increased the modulus. Similar results were reported by Köster and Rosenthal⁶¹ on 72-28 brass, whose modulus was decreased by cold-drawing. Upon annealing, the modulus increased, one third of the initial decrease being recovered prior to recrystallization and the remaining two thirds during recrystallization. With increase in

grain size above the recrystallization temperature, the modulus increased still further. In a further paper, Köster⁶⁸ found that Young's modulus in aluminum had a variable behavior, depending on the amount of working, and also that these changes were about twice as great in magnitude in 99.99 per cent aluminum as in commercially pure (99.5 per cent) aluminum. He attributed these effects to the same factors as Kawai;⁶⁰ i.e., internal stresses and fiber structure. Kersten⁶² has also discussed the effect of internal strain on the elastic modulus, chiefly in relation to ferromagnetic materials, and the variations of elastic modulus with drawing. Kuntze⁶⁴ has contributed a similar paper on copper as has Baldwin.⁶⁷

An important question in regard to the effect of working on Young's modulus has been raised by Galibourg,⁶³ who found that the modulus of annealed nickel is higher than that of the same metal cold-worked (and aged), *provided* the stress was figured on the basis of the original section after the first working (by pulling). If, however, the stress was computed from the section existing before the final pulling, the modulus of the cold-worked nickel was greater than that of annealed metal. Thus he cites the data shown in Table 2.

TABLE 2.—*Effect of Method Employed in Calculating Stress on Modulus of Nickel*⁶³

MATERIAL	YOUNG'S MODULUS LB. PER SQ. IN.
Annealed nickel.....	31,650,000
Cold-worked and aged nickel, stress based on initial section.....	30,500,000
Cold-worked and aged nickel, stress based on final section after four pullings.....	32,200,000

These differences are fairly small and would be of little importance except in work demanding high precision. They may also arise from other causes than those suggested by Galibourg. Another anomaly concerning the modulus was found by Lea and co-workers⁶⁶ in an extensive study of the effect of cold-working and annealing on the properties of

thin-walled brass tubes. They found that the modulus in direct tension and the modulus in indirect compression of hard and half-hard tubes varied in an erratic fashion with annealing temperatures (up to 710°C). This is similar to results by other authors cited above. However, the modulus determined by flexural methods underwent no such variations, but rose steadily and uniformly as the annealing temperature was increased above room temperature. This "flexural" modulus was also always 7 to 10 per cent greater than the "tensile" modulus. Perhaps this difference arose because of experimental difficulties, because of insufficiently rigorous mathematical analysis or because of the presence of fibering.

Vater⁶⁶ studied the influence of cyclic stresses of two types, alternating bending and tensile, on the elastic moduli of spring steel and Elektron. His results are not conclusive but indicate that cyclic stresses probably decrease the modulus, particularly in the presence of over-stressing.

It seems on the basis of the results cited that Young's modulus generally decreases with cold-working, increases somewhat with aging or a strain-relieving anneal (for cold-worked material) and increases considerably with recrystallization. Behavior for anneals above the recrystallization temperature seems to vary for different materials and is generally erratic, depending largely on the type and extent of cold-working.

Chemical Composition, Alloying

Undoubtedly, the most extensive work on the effect of the composition of alloys on Young's modulus has been done by Nishayama⁷ and Guillet,² although there have been many other contributors to the field, a few of whom are mentioned in references 67, 10, 68, 1, 39, 69, 70, 71, 72 and 75.

In the range of terminal solid solutions,

all workers are in agreement that no unusual variations exist in Young's modulus as a function of composition, such as occur in hardness or electrical conductivity.

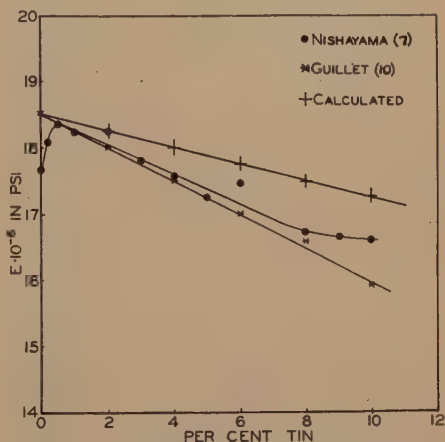


FIG. 4.—MODULUS OF ELASTICITY OF ANNEALED COPPER-TIN ALLOYS AS FUNCTION OF COMPOSITION.

Experimental data of Nishiyama and Guillet lie under those calculated from the rule of mixtures.

If the modulus is plotted against composition in these ranges, a sensibly straight line results, which will obey the simple rule of mixtures (Cu-Zn, Pt-Ir, Pt-Rh, Cu-Ni, Ag-Au, Al-Mg, Mg-Al), or lie under the line representing the rule of mixtures (Cu-Sn, Cu-Al, Fe-Ni) (Fig. 4). The data for at least one of these systems (Cu-Al), which do not give a linear relationship, can be made to lie on a straight line if the abscissas are plotted as *volume per cent* rather than the usual *weight per cent*.² There is very little agreement among the data, however, as to the exact numerical value of the modulus for any specific composition, thus Nishayama's data are quite different from those of Guillet. The reason does not lie in slight differences in composition but probably in thermal and mechanical history and the fact that Guillet used the double pendulum method of LeRolland and Sorin to deter-

mine E while Nishayama used beam flexure.

In alloys where solid solubility is limited, the appearance of a second phase* with increasing additions of the second element usually causes no change in the shape or slope of the curve for modulus versus composition, providing all alloys are in the fully annealed and slowly cooled (equilibrium) condition.^{2,72†} This means that the modulus can still be well approximated by the rule of mixtures but usually does not hold, however, if the second phase is an intermetallic compound of the type having homopolar bonding (Cu_9Al_4 , Cu_7Zn_8 , $\text{Cu}_{31}\text{Sn}_3$, etc.).^{2,71} These homopolar compounds have much higher moduli (20 to 40 per cent) than those given by the rule of mixtures.

Information is rare on the change of modulus with composition in alloy systems of the mechanical mixture type (eutectic, eutectoid, peritectic, etc.). Guillet⁶⁷ says that the variations in modulus are essentially linear, and that the curve for modulus versus composition does not consist of the two straight lines meeting at a maximum at the eutectic composition, as it does for hardness, elastic limit and tensile strength. He gives the Zn-Cd system as an example. Perhaps this is true for a simple system such as Zn-Cd, but it is not true for the more complicated systems, Cu-Zn, Cu-Sn and Cu-Al, as shown by Guillet.² In these three systems the rule of mixtures seems to be obeyed except when interrupted by homopolar compounds. Köster,³⁹ working with the same systems, was unable to find any relation

between E and composition, although he does state that the phase with the lowest symmetry has the highest value of E , while Portevin and Chevenard⁷⁰ conclude that the elastic modulus of an alloy varies in an almost linear fashion with composition, the effect of structure being entirely secondary. Cast iron is an apparent exception and is discussed in a separate section.

Much more evidence is needed on the effect of composition and microstructure of alloys on Young's modulus before positive conclusions can be drawn. Enough evidence exists, however, to support Guillet's⁶⁷ contention that one cannot hope to greatly change the modulus by the simple addition of one alloying element, as can be done with other properties. No evidence was found in the literature to support his other contention that more is to be expected from ternary and quaternary alloys than from the simpler binary systems.

Heat-treatment, Age-hardening, Ordering

Apparently Masing and Haase³⁴ were the first to show that the modulus of elasticity underwent a pronounced change during the solution heat-treatment and subsequent precipitation in the age-hardening process. They found that the torsion modulus of 2.5 to 3.0 per cent beryllium copper increased almost linearly with the time of aging at 200°C. but at 400°C. it rose rapidly to a maximum in one hour, after which it dropped off. The increase in the modulus during aging was 26 per cent. They used this to confirm their belief that age-hardening was due to the precipitation of a new phase from supersaturated solid solution. Guillet,² using a similar alloy and treatment, found an increase during aging of only 6 per cent in Young's modulus. In a previous paper Guillet⁷² had found that in annealed Be-Cu alloys the modulus was a linear function of beryllium content up to 18.5

* Provided this second phase is a solid solution, a pure metal or an intermetallic compound having metallic bonding (CuZn , Al_2Cu , etc.)

† This has led Guillet⁶⁷ to raise the question: What may be the elastic limit of a binary alloy formed of two phases, a and b , of which the elastic limits are Ea and Eb , Ea is less than Eb ? In reality, ought it not always preserve the value of Ea , which is the smallest? Practically this is not so and is explained by the structure itself.

Portevin has analyzed this question from the theoretical point of view.

per cent beryllium. On the basis of these results one might expect similar effects for all alloys capable of age-hardening. Evidence from only one other system,

um at the eutectoid composition, decreasing on either side of it. Reannealing returns the modulus to its initial value except when the composition approaches

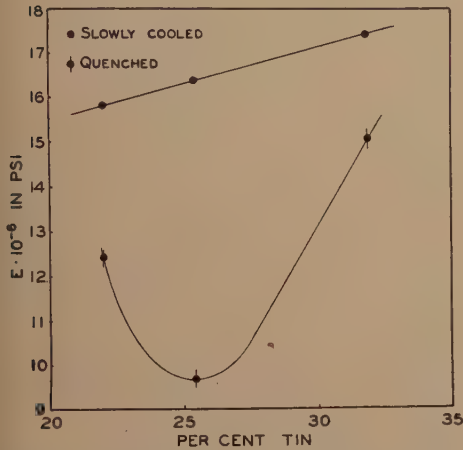


FIG. 5.—EFFECT OF COOLING RATE ON MODULUS OF ELASTICITY OF COPPER-TIN ALLOYS IN REGION OF EUTECTOID.⁷⁶

Al-Be, is available³ and these alloys show only the slightest change in E upon aging. Strangely enough, Guillet,² in his extensive thesis on Young's modulus, worked with numerous alloys capable of being age-hardened but investigated the effects of age-hardening in only two of them, as mentioned above, Cu-Be and Al-Be.

Other types of transformations that are affected by thermal treatment have been investigated. One of the most interesting of these is the suppression of the eutectoid transformation in Cu-Al and Cu-Sn alloys by quenching.^{2,75} These alloys, when quenched from above the eutectoid temperature, develop a metastable structure, which in the Cu-Al alloys is similar to the martensitic structure produced in steel by quenching. In both alloys a considerable drop (50 per cent) occurs in E when the alloy is quenched rather than slowly cooled (Fig. 5). Intermediate cooling rates give intermediate values of E (Fig. 6). This effect is a maxi-

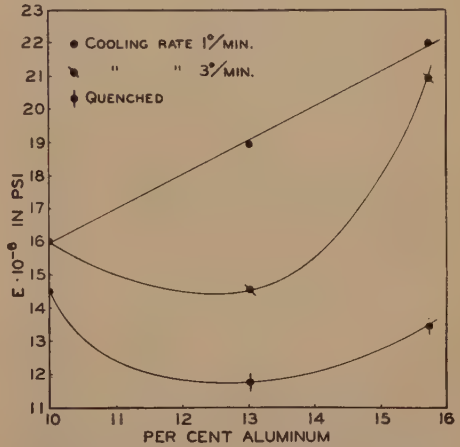


FIG. 6.—EFFECT OF COOLING RATE ON MODULUS OF ELASTICITY OF COPPER-ALUMINUM ALLOYS IN REGION OF EUTECTOID.⁷⁶

that of a homopolar compound.^{2,75} These compounds are hard, brittle, and poor conductors of heat. Hence, the initial quench is believed to cause microscopic cracks in the structure, which also tend to decrease E and which prevent the return of the modulus to its initial value upon annealing. This decrease in Young's modulus in these alloys upon quenching is also revealed when the alloys are chill cast rather than sand cast and must be taken into account in bell founding, because of its effect on tone quality.

Incidentally, Benedicks^{68,74} has explained these effects on the basis of a deformed lattice and offers further experimental evidence in support of his theory.

Another type of thermal transformation where the change in modulus has been investigated is the order-disorder transformation. Such transformations occurring in the Au-Cu, Ag-Cd, Cu-Zn systems have been studied by Köster,³⁹ Guillet,² Siegel,¹⁰³ Guillet and Portevin⁷⁵ and others. Guillet found that Young's modu-

lus did not change appreciably with the appearance of ordering although the hardness and electrical conductivity changed considerably. Köster, on the contrary, feels that measurements of E constitute an excellent method for investigating phase transitions, including order-disorder phenomena. This disagreement may have arisen because the two men used different methods of determining the modulus. Certainly more work is needed on this aspect of the problem before a definite conclusion will be available.

Heat-treatment and Quenching of Steel

The heat treatment and quenching of steel was one of the most fertile fields of investigation for the earlier workers on Young's modulus but, queer as it may seem, the writer does not have a single reference to the specific problem of the variation in E with the heat-treatment of steel by quenching. This is probably because most authors have been superficially in agreement for the past 50 or 60 years that Young's modulus is virtually unaffected by quenching or quenching and tempering. Most of the general evidence cited thus far seems to support this contention, although it is belied by the behavior of the Cu-Al alloys, which undergo a similar martensite-like transformation upon quenching. It might be interesting to investigate variations in Young's modulus among the various isothermal transformation products of austenite and also during the quenching and tempering (aging) in a steel such as high-speed. Historical evidence argues against any great variations but the problem would be of considerable theoretical interest.

Effect of Temperature

Probably more papers are devoted solely to the effect of temperature on E than to any other single aspect of the entire subject. Generally, the papers are in good

agreement upon the fact that E decreases as the temperature increases.* Upon the specific magnitude of this effect the individual authors are in poor agreement. Many of the papers are vitiated because of ignorance of, or inattention to, metallurgical details, chief among which are aging, recrystallization and grain-growth phenomena. These omissions are more frequent and serious in older papers. Much of the disagreement on results may also be attributed to the wide variety of methods used in the determination of the modulus and the injudicious comparison of values determined by widely different methods, and even comparison of different elastic moduli.

Reference has already been made (p. 3) to the importance of the temperature effect on the elastic modulus and to the fact that the formula of Andrews⁵² shows the necessity of stating the temperature at which E is to be determined. The practical importance of the temperature dependence of Young's modulus has been recognized by the Bureau of Standards and the aircraft industry in several papers^{76,77,78} where the variation in E has been determined over the temperature range commonly encountered in operation of aircraft instruments.

Several papers on the temperature effect had already appeared by 1900, when Thomas⁷⁹ published one devoted to a criticism of previous methods used for determining the elastic coefficient of cast iron at various temperatures. He also discussed sources of error and pointed out, quite correctly, that temperature has an effect that depends upon the duration of exposure to it. Years later (1923), Schaefer⁸⁰ stated that measurements of the temperature variation of

* Köster³⁹ claims that metastable phases and some intermetallic compounds such as AgCd and AuCu have a modulus that increases, rather than decreases, with temperature, while Kersten³⁶ has shown that certain low coefficient of expansion alloys have a zero temperature coefficient of elasticity.

the elastic constants had been made in Germany by Katzenelsohn as early as 1887. One of the interesting questions was raised by Walker⁸¹ in 1907, who suggested that the modulus would have different values at elevated temperature, depending upon whether it was raised to the temperature by passage of an electric current or whether it was indirectly heated. In a series of papers, Dodge^{82,83,73,84} showed that E was the same regardless of the manner in which the specimen was heated, and also contributed information on the magnitude of the temperature effect on E . Dodge also concluded that by thorough annealing the metal can be brought to a cyclic state in which the modulus becomes a function of temperature, and that the modulus of a metal decreases with increasing temperature, the rate of change increasing with the temperature. There is still some indication⁸⁵ that Walker may have been partly correct, if one is dealing with a ferromagnetic material and the heating current is such as to cause magnetization of the material, although the effect is very small. Nakamura⁹⁴ has shown the desirability of making determinations of the modulus of Fe, Ni and Co in a constant magnetic field even at high temperatures.

The general form of the expression¹⁹ showing the temperature dependence of E is:

$$E = E_1 e^{b_1 t}$$

where E is Young's modulus, E_1 and b_1 are constants and t is the temperature. If the torsion modulus is desired, n is substituted for E . The constants, and also dE/dt (or dn/dt), have been evaluated for many common metals and alloys.^{18,36,86,87,88,29,89,40,90,80,30,91,6,92} Other temperature relationships of Young's modulus are shown by Mallock,⁶ who has also presented a theory of temperature action.²⁹ The change in E down to very low temperatures has been investigated⁸⁸ as has the temperature effect in single crystals.^{30,93} Two papers,^{30,90}

showing that previous history of the specimen is very important, confirm the data of Dodge already cited.

In conclusion, it is probably safe to say that the effect of temperature on the elastic modulus E has been sufficiently investigated so that data of some sort are available on most common metals and alloys.

Effect of Pressure

Data are almost completely lacking on the effect of pressure. Bridgman has published several papers on the effect of pressure on the rigidity of several materials. Only one paper¹⁴ was reviewed but the results indicate that pressure has very little effect. Apparently the rigidity of steel increases with pressure while with glass rigidity decreases.

Degree of Magnetic Saturation

One of the complicating items from the standpoint of the development of a theory of what constitutes Young's modulus is the fact that in the ferromagnetic metals and alloys the degree of magnetic saturation affects the observed value of the modulus. It is observed⁸⁵ that E is greater in the magnetically saturated than in the demagnetized state. The various authors do not agree on the magnitude of the increase but are in agreement that the effect is the greatest on nickel and iron-nickel alloys.

Siegel and Quimby²³ found the percentage increase in Young's modulus in nickel to be 6.7 per cent between the demagnetized and the saturated state at 23°C., rising to 18.7 per cent increase at 185°C. and decreasing to zero at the Curie point. These results are generally confirmed by Nakamura,⁹⁵ who reported that for Fe-Ni alloys containing less than 30 per cent Ni the effect was very small, reaching its maximum at 50 per cent Ni but generally being smaller than for pure nickel. He also found that Young's

modulus for iron and cobalt was almost independent of their magnetization, which is somewhat at variance with theory and the results of others. Even in a material such as Permalloy, Siegel and Rosin⁹⁶ found that the increase between zero and complete magnetization varied only between 0.11 per cent and 0.26 per cent, depending upon the previous treatment accorded the specimen.

The theory of this effect has been discussed extensively by Kersten,^{85, 62} Yamamoto,⁹⁷ and Siegel.^{23, 98} Siegel favors the theory proposed by Akulov⁹⁸ while Kersten favors that of R. Becker.⁹⁹ The factors involved in the theoretical development are the elasticity, magnetostriction and the initial state of internal stress of the material. Much more work is needed on the effect of magnetization on Young's modulus.

Method of Determination, Size of Specimen, Magnitude of Loading

Method of determination, size of specimen and magnitude of loading all apparently affect Young's modulus, but precise information is scarce.^{20, 37, 38} They have all been discussed in the section on the experimental determination of Young's modulus.

Discontinuities in the Metal, Graphite in Cast Iron

As mentioned, metallographic structure does not greatly affect Young's modulus unless the structure is metastable or unless discontinuities such as quenching cracks or blowholes are present. Graphitic materials are a decided exception to this, it being possible to vary the modulus over a wide range merely by varying the size, shape and distribution of the graphite particles.

Gray cast iron is the commonest of these graphitic materials. The structure of gray iron is essentially a pearlitic matrix in which the graphite particles

are distributed. The size, number and distribution of the graphite flakes can be varied over a wide range by suitable changes in foundry practice. The matrix of the gray iron is actually steel and hence would remain the same for considerable variations in analysis, and would be expected to have a modulus that could not be varied appreciably. Hence, variations in the modulus may be attributed, according to Meyersburg,¹⁰⁰ to variations in the fraction of the cross-sectional area that carries the load, because it is only the steel matrix that can carry or transmit load. He illustrates this schematically and also by reference to irons having different amounts of combined carbon.

Thum and Ude¹⁰¹ have studied this problem in a very ingenious manner. They cut tensile specimens from steel sheet, which they perforated with regularly distributed holes (slots), the dimensions of which varied from one specimen to another, the section remaining between the holes of the same row being constant for all the specimens. The tensile curves obtained from these specimens (plotting total load as ordinate and elastic elongation as abscissa) show that the modulus decreases when the dimension of the holes is increased perpendicularly to the tensile load. They then studied a series of cast irons, in which the graphite varied from almost stringers to rounded particles, in order to show the analogy with the preceding specimens, the holes being replaced by the graphite. The curves obtained classified themselves in the same order as the slotted sheet specimens.

Graphitic materials other than gray iron have been studied carefully by Schwartz and Junge.¹⁰² Their conclusions are in general agreement with the results on gray iron. In addition, they found that graphite in flake form decreased E much more than an equal amount of temper carbon (malleable iron) and that there was a linear relationship between graphite

content and E provided all the graphite was present as temper carbon and none had been recombined by heat-treatment. Also, that when the graphite existed only as temper carbon—that is, when the metallic matrix is interrupted only by approximately spherical voids and/or inclusions—the modulus is directly proportional to the amount of metallic phase in a unit volume. Schwartz and Junge even proposed that these principals might form the basis for quantitatively expressing graphite form.

CONCLUSIONS

The available information on Young's modulus has been critically reviewed and summarized. Apparently many of the data are inaccurate or contradictory and should be critically appraised before use.

Most attempts along routine channels (alloying, heat-treatment, working) to change the elastic moduli are foredoomed to failure. If it is desired to change E of a given material permanently, recourse must be had to purely mechanical means, such as the development of texture, combination or incorporation through suitable design of other substances with the desired material, or by increasing the porosity of the material itself. This is certainly not a wide or promising list of methods whereby Young's modulus can be varied, but it must suffice for the present.

SUMMARY

The literature on Young's modulus has been reviewed and critically appraised. It was found that methods of calculating the modulus from theoretical considerations are scarce although progress is being made. A number of empirical relations correlating the modulus with other properties, such as atomic volume and specific heat, have been developed, but the best is that of Andrews, who has shown that for

any element the modulus is a function of atomic volume, melting point and the temperature.

Experimental methods for the determination of Young's modulus were found to fall into two classes: (1) static, such as the tension test and beam flexure; and (2) dynamic, such as the twin pendulums and oscillatory or vibratory methods. The difficulties and advantages of the various methods are enumerated and comparisons made. There is no "best" method for determining the modulus.

The many factors that affect the magnitude of Young's modulus were examined. Crystallographic effects seem the most important because of elastic anisotropy. Cold-working reduces the modulus while stress-relieving and process anneals tend to increase it. The effect of alloying is directly proportional to the amount of alloying element added, provided the alloys are in the fully annealed condition. Microstructure has little effect unless homopolar compounds are involved, although age-hardening and suppressed eutectoidal transformations seem to affect the modulus in certain cases. Agreement is poor on the effects of heat-treatment of alloys. Temperature exerts considerable influence on the value of the modulus, the modulus decreasing with increasing temperature. Considerable data are available on the effect of temperature, although individual values may not agree well with each other. The degree of magnetic saturation affects the modulus of ferromagnetic materials. It is shown that discontinuities in the metal, such as cracks, blowholes, or graphite in cast iron, lower the modulus considerably.

ACKNOWLEDGMENTS

The writer wishes to acknowledge his indebtedness to Prof. E. S. Fabian and Dr. K. L. Hertel, of the University of Tennessee, for their critical review of this paper.

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DISCUSSION

(R. M. Brick presiding)

J. T. NORTON.*—Two problems connected with Young's modulus have been of considerable interest to us recently. One has to do again with X-ray stress measurement. I do not want to bore you with this, but it represents a puzzle which somehow or other has to be solved.

In the X-ray measurement, of course, we measure strains, and in order to convert those strains into stresses, we must have the elastic contents of the material. In making the measurements by X-rays, we are measuring strains in a certain crystallographic direction; but the crystals that are being measured—that is, the crystals that contribute to the diffraction pattern—do not have a common direction parallel to the stress, and that brings up the question of what should be used for the elastic modulus.

The problem has not been solved theoretically but in practice we find that for some metals if we take the modulus determined in the normal way on a polycrystal material, the values of stresses measured by X-rays agree with those measured mechanically.

In some other metals, the situation is quite different, and there may be values of stresses that perhaps are 100 per cent away from the true values of stress. The only way in which we have been able to get around this difficulty so far has been to make an actual calibration on the material to be investigated. That is a nuisance, but seems to be the only way.

I certainly would like to have somebody solve the problem of the elastic deformation of a polycrystal material with a random orientation of the crystal grains, particularly when crystals are elastically anisotropic.

Whether we want to consider the stresses equal in all the grains or the strains equal in all the grains, or something in between, which probably is the true situation, I frankly do not know.

In connection with Young's modulus I have come across a suggestion in the literature

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that for wires of small diameter of the same material the Young's modulus depends upon the diameter of the wire. I should like to know whether that is really true, or whether it is in effect due to surface or something that has not so far been recognized. It would be of considerable interest theoretically if that were actually so.

G. H. BOSS.*—While at school, I did a little thinking on Young's modulus. At that time it seemed to me that it should be possible to calculate Young's modulus from some relation among the constants of the crystalline state of the metal. On this basis, then, I tried to set up a correlation between the force required to separate the atoms in the crystals as measured by the modulus and the energy required to separate them as measured by the specific heat, atomic volume and the linear coefficients of expansion. While many metals would fit into a formula involving these constants, a few would not. Gold and silver do not conform in any way; the metals of the iron and platinum groups seem to follow a law of their own. Perhaps someone else may find this idea worth pursuing.

D. J. MACK (author's reply).—I sympathize wholeheartedly with Professor Norton on the problem of what value to use for the elastic modulus when endeavoring to deduce stress values from strain measurements on polycrystalline material. We have been faced with a similar problem involving very thin, heavily cold-worked sheet; i.e., the calculation of stresses in certain instrument components from strain measurements where an element of the component can be treated as a cantilever beam and the result can be integrated to include the entire component part. If we assumed a "reasonable" value for the modulus, the stress values would frequently be of impossible magnitude; while if we reversed

the process in other cases and calculated the modulus from assumed stress values that seemed probable, the modulus would have an entirely unreasonable value. We realize, of course, that our assumptions regarding the element as a cantilever beam or the summation to include the entire instrument component may be in error, but so far we have not been able to locate it and have become increasingly convinced that the modulus may actually have seemingly unreasonable values, because of the thinness of the material and the heavy cold-working it receives. Unfortunately, we cannot calibrate the material beforehand, as Professor Norton does, because fabrication into the instrument component changes the modulus.

I have had no experience with the effect of wire diameter on Young's modulus as reported in the literature but some work we have done indicates that there is a similar effect for very thin sheet material, 0.0012 to 0.0100 in. thick. The effect is apparently real and is associated with the elastic anisotropy in the very thin sheet caused by the extensive working it receives. However, there is also a pronounced edge effect when the modulus of the thin sheet is determined by the usual tensile method. We have tried using drawn tubes having the same wall thickness as the sheet in an effort to eliminate this edge effect in the tensile method but the work has not been carried far enough to obtain conclusive results.

In endeavoring to compute Young's modulus from the physical constants of a material, Mr. Boss encountered the same difficulty as others (for example, references 41 to 44, 49 to 52 in the paper) who have attempted similar calculations; i.e., the results are in good agreement with experimental values for some materials and poor for others. Apparently the best approach for calculation of the modulus is that of quantum mechanics as used by Fuchs,⁴⁶⁻⁴⁸ although I believe there is probably a theoretical basis for the empirical relation between physical constants and Young's modulus developed by Andrews.⁵²

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Relative Triaxial Deformation Rates

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(New York Meeting, October 1945)

EXPLORATORY WORK

THE related subjects of preferred orientation, directionality in physical properties, and earing tendencies of wrought metal

knowledge thus accrued, no simple quantitative correlation of directionality and earing tendencies has yet been found. In a sense, this is not surprising. The formation

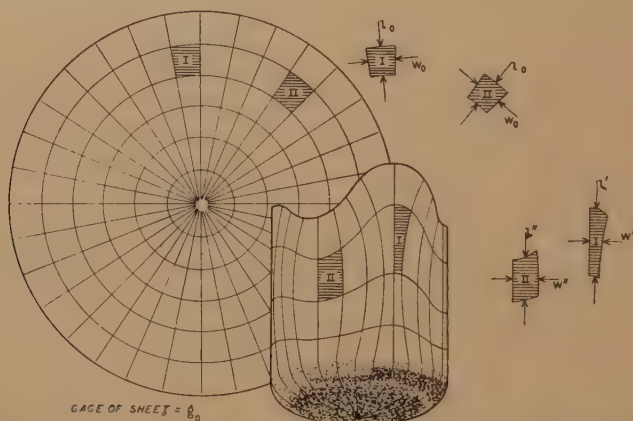


FIG. 1.—BLANKED DISK WITH SCRIBED POLAR PLAT AND DRAWN CUP WITH EARS. Showing directionality in relative rates of deformation in the three principal directions.

strip have attracted the attention of metallurgists to such an extent that in the past 20 years hundreds of researches have been published on this one general problem. The anisotropy of tensile strength and elongation have been exhaustively studied in their relationship to the occurrence of ears in cups drawn from strip^{1-20,29} and, to a lesser extent, yield strength^{7,11,17} and stress-strain curves¹⁵ have been investigated. Despite the tremendous fund of

of ears in a drawn cup clearly is a special phase of the general study of metal flow; in particular (as will be brought out in the course of this paper), ears are due to anisotropy in the rates of deformation of the metal in the radial, circumferential, and "thickness" directions of the original blank. It would be difficult to effect a correlation between earing tendency and a property that may be completely independent of the flow of metal, or at best related to metal flow in an exceedingly complex fashion. Yet, it is this correlation that has been attempted; tensile strength and elongation are attributes of metal rupture, a phenomenon that has quite admirably been shown to be distinct from the phenomenon of metal flow,²¹ while yield strength and stress-strain

Manuscript received at the office of the Institute June 14, 1944. Listed for New York Meeting, February 1945, which was canceled. Issued as T.P. 1808 in METALS TECHNOLOGY, September 1945.

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¹ References are at the end of the paper.

functions when obtained by measuring the interdependence of load and elongation are confined to uniaxial stress-strain conditions.

DIRECTIONALITY IN TRIAXIAL DEFORMATION RATES

Ear formation can be studied by the standard device of scribing a plat or grid on a blanked disk and following the deformation of this plat as the disk is drawn into a cup.

Fig. 1 is a sketch made from a fully drawn cup. The cup itself was drawn from 100 per cent cubically aligned soft copper strip; i.e., from strip all of whose grains have a (100) plane parallel to the rolling plane and a [001] axis parallel to the rolling direction. The cup sidewall was of the same thickness as the original blank.

Two elements, I and II, have been selected on the original disk; their dimensions, because of the symmetry of the plat, are the same: viz., l_0 , w_0 , and g_0 .

The final dimensions of element I lying in the eared portion of the cup are l' , w' , and g' , while those of element II lying in the portion of the cup containing the trough are l'' , w'' , and g'' . It is obvious from the sketch that $l' > l''$, $w' < w''$. (Further, $g' = g''$, this equality being due to ironing.) The deformation suffered by the two elements are $\ln l'/l_0$, $\ln w'/w_0$, $\ln g'/g_0$, and $\ln l''/l_0$, $\ln w''/w_0$, and $\ln g''/g_0$, respectively, in which

$$\ln \frac{l'}{l_0} > \ln \frac{l''}{l_0}$$

$$\ln \frac{w'}{w_0} < \ln \frac{w''}{w_0}$$

and

$$\ln \frac{g'}{g_0} = \ln \frac{g''}{g_0}$$

whence it is seen that the deformations in the three "principal" directions proceed at different rates in the case of the two elements; i.e., these elements have displayed directionality with respect to triaxial deformation rates.

It must be admitted that the actual course of deformation throughout the entire cupping process may be quite complex, yet the fact remains that somewhere

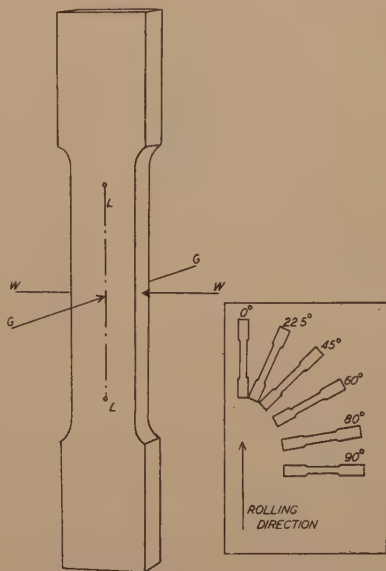


FIG. 2.—EXPERIMENTAL PROCEDURE FOR DETERMINING ANISOTROPY IN RELATIVE RATES OF CONTRACTION OF WIDTH AND GAUGE.

Standard tensile specimens milled from strip at different angles to rolling direction were pulled in tension to arbitrary values of elongation in a 2-inch length (LL) while width (WW) and gauge (GG) were measured.

during the process such directionality has been evidenced.

EVIDENCE OF DIRECTIONALITY IN DEFORMATION RATES IN THE THREE PRINCIPAL DIRECTIONS FOR THE STRESS SYSTEM: SIMPLE UNIAXIAL TENSION

The experimental procedure is graphically depicted in Fig. 2. Standard tensile specimens were milled from strip at various angles to the rolling direction. The specimens were loaded to a series of arbitrary values of elongation (usually every 5 per cent from 0 per cent to fracture) and the dimensions of the width (WW) and gauge (GG) were determined

with micrometers. The values of width and gauge so determined were recorded in terms of unit width and unit gauge—i.e., in terms of the ratio of the width or

direction suffers a change in external shape similar to any metal that is being cold-rolled; i.e., it elongates in one direction, contracts in another direction normal to the

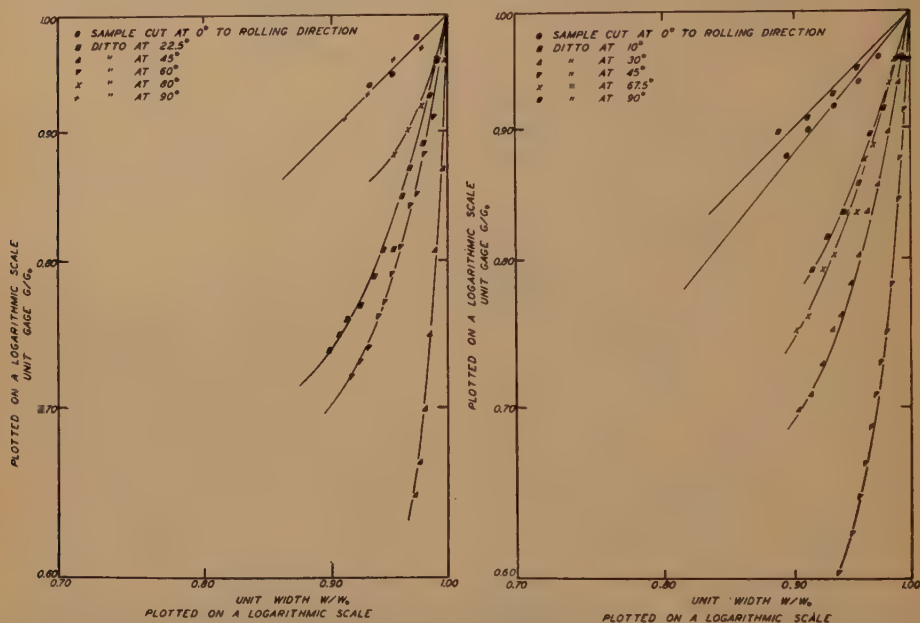


FIG. 3.—CONTRACTION OF UNIT WIDTH AND UNIT GAUGE DURING TENSILE TEST OF TWO SAMPLES OF 100 PER CENT CUBICALLY ALIGNED COPPER STRIP.

Test specimens taken at different angles to the rolling direction.

gauge at an arbitrary elongation to the original width or gauge before testing. These values for two 100 per cent cubically aligned annealed copper strips on 0.025-in. gauge are plotted logarithmically in Figs. 3a and 3b. It is at once apparent that the rate of contraction of gauge with respect to that of width is a function of the angle between the specimen axis and the rolling direction. In the specimens cut at 0° to the rolling direction, the gauge and width contract at an equal rate, but as the angle between the tensile specimen and the rolling direction increases, the gauge contracts more rapidly until at 45° the gauge contracts about 30 times as fast as the width at the beginning of the test. From 45° the rates tend once more to an equality.

The tensile specimen at 45° to the rolling

direction suffers little deformation in a direction normal to the first two.

X-ray analysis of the specimen cut at 45° to the rolling direction and pulled in tension and of a specimen cut at the same angle and then cold-rolled reveals two very similar pole figures (Figs. 4a and 4b), thus extending the general law that similar deformations produce similar crystallographic pole figures. Of especial interest, however, is the fact that both pole figures have been produced by a simple rotation of the octahedral poles about the transverse $[01\bar{1}]$ axis. This rotation can be produced most simply by equal and simultaneous slip on the slip systems $(111)[10\bar{1}]$ and $(111)[1\bar{1}0]$. Such a system acts as if it were the simple slip system $(111)[2\bar{1}\bar{1}]$ (Fig. 4c). In this case, the pole of the slip plane P,

the slip direction D , the tensile axis (or rolling direction) L of the specimen and the gauge axis G all lie in the same plane, while the width axis W lies normal to this plane

will suffer no change while the relation between change of gauge and of length is according to the equation:

$$d \ln L = -d \ln G$$

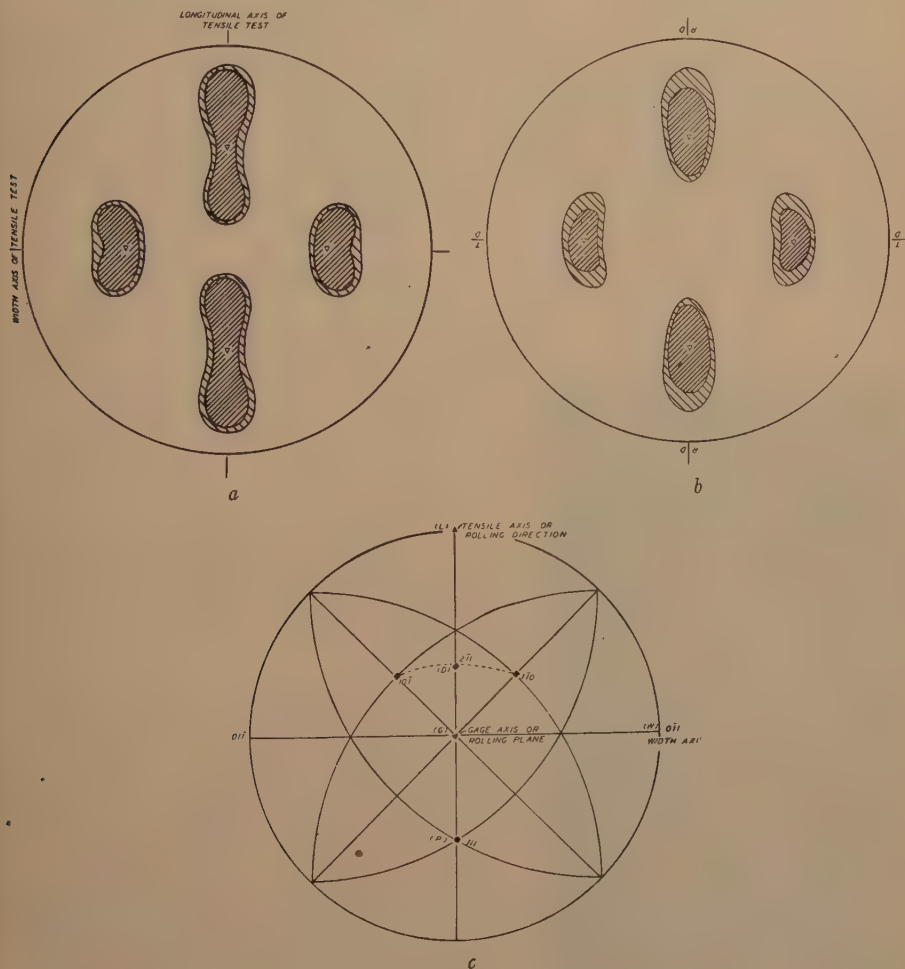


FIG. 4.—POLE FIGURES AND STEREOGRAPHIC PROJECTION.

a. Octahedral pole figure of 100 per cent cubically aligned copper cut at 45° to the rolling direction and pulled in tension to an elongation of 60 per cent. Triangles indicate starting orientation.

b. Octahedral pole figure of soft polycrystalline copper cold-rolled 43 per cent reduction from a starting $(001) [110]$ orientation, obtained by cutting a strip at 45° to the rolling direction of annealed 100 per cent cubically aligned copper.

c. Stereographic projection showing slip systems operating to give rotation shown in *a* and *b*. (Fig. 4*c* and 5*a*). It should be clear from Fig. 5*a* or 5*b* that as the slip direction rotates toward the tensile axis in their common plane the width of the specimen

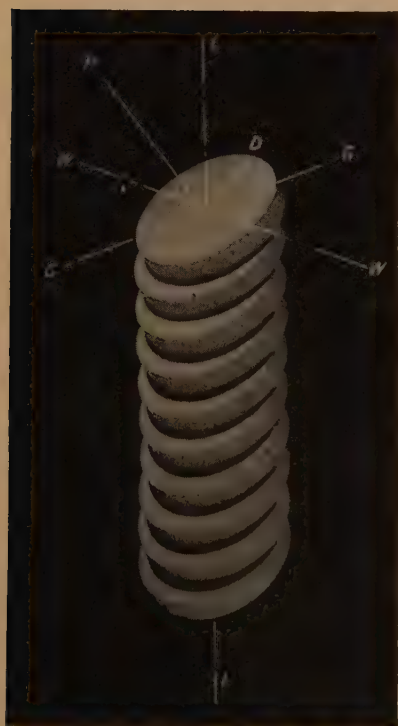
Thus the curves obtained in Fig. 3*a* and 3*b* for the samples cut at 45° to the rolling direction are explained by the manner in which the crystallites deform.

EVIDENCE OF DIRECTIONALITY IN
DEFORMATION RATES IN THE
THREE PRINCIPAL DIRECTIONS
FOR THE STRESS SYSTEM:
SIMPLE UNIAXIAL
COMPRESSION

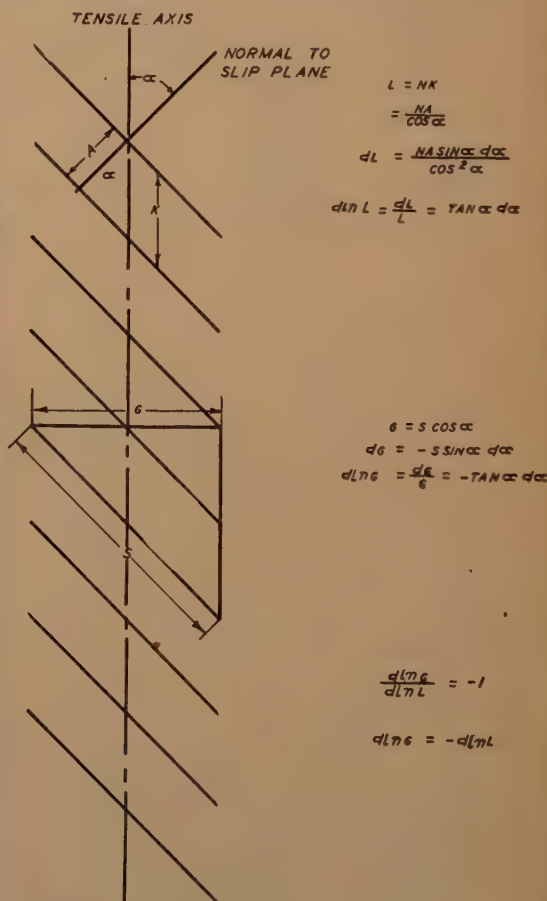
It would have been very interesting indeed if the experiments described in the previous section and depicted in Fig. 2 could have been repeated on a similar set of specimens using compression instead

of tension. Physical limitations, of course, prevent the execution of such experiments. In an effort to approach the condition of simple uniaxial compression, however, the following experiments were conducted.

Two strips, one piece at 0° and the other at 45° to the rolling direction, were cut from 0.040-in. thick copper that had been cold-rolled in the neighborhood of 96 per cent. They were wrapped around mandrels to form tubes about 1.0 in. in diameter;



a



b

FIG. 5.—MODELS.

a. Model showing relationship of slip system for specimen cut at 45° to rolling direction. Tensile axis L , width axis W , gauge axis G , slip-plane normal P , slip direction D .

b. Section view of model shown in a. Width axis is perpendicular to plane of paper. Distance between slip plane is A , length of slip plane is S , and angle between tensile axis and normal to slip plane is α , number of slip planes is N . Slip direction lies in slip plane in plane of paper and moves in plane of paper toward tensile axis as deformation proceeds.

annealed, and the seams were butt-soldered. The microstructure of the copper when annealed was what under normal conditions would be described as 100 per cent cubically aligned; i.e., a $[001]$ axis was parallel to the old rolling direction and a (100) plane was parallel to the old rolling plane of the strip. In its new form, however, the tube that was formed from the specimen cut at 0° to the strip-rolling direction had a $[001]$ axis parallel to the longitudinal axis of the tube, a $[100]$ axis parallel to the radial axis, and a $[010]$ axis parallel to the tangential axis. The other tube had a $[110]$ axis parallel to the longitudinal axis, a $[001]$ axis parallel to the radial axis, and a $[1\bar{1}0]$ axis parallel to the tangential axis. These conditions are illustrated in Fig. 6. The tubes were pointed and then sunk in a series of passes, each giving a 1 to 2 per cent reduction in diameter. In this manner an element in the wall of the tube at the exit side of the die was subjected to a small longitudinal tensile stress, a small radial compressive stress, and a large compressive hoop stress.* The simultaneous diameter and thickness changes are recorded in Fig. 7. Also in Fig. 7, a line giving the expected dimensional changes for isotropic copper† is drawn from the starting values of both tubes. It is at once apparent that the sample tube formed from a strip cut at 0° to the rolling direction behaves as if iso-

tropic, while the other tube gives much higher thickness values than those expected from isotropic copper. While the data in Fig. 7 are actually portions of curves, they

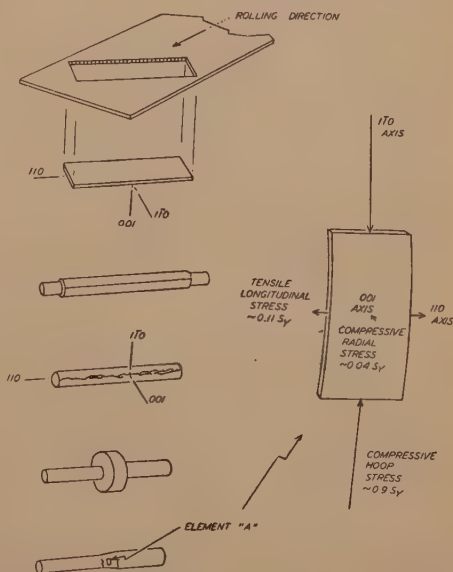


FIG. 6.—EXPERIMENTAL PROCEDURE FOR DETERMINING DIRECTIONALITY IN TRIAXIAL DEFORMATION RATES FOR 100 PER CENT CUBICALLY ALIGNED COPPER FOR STRESS SYSTEM APPROACHING SIMPLE UNIAXIAL COMPRESSION.

Specimens were cut from hard-rolled strip, wrapped around mandrel and annealed. The seam was butt soldered, and the resulting tube was sunk in a series of passes, giving 1 to 2 per cent reduction in diameter. The resulting stress system (at 1 to 2 per cent reduction) for a small element is illustrated.

* For isotropic copper, the stress required to sink a tube 1 to 2 per cent is about 11 per cent of the yield strength of the metal, so that according to either the Mohr or von Mises equation, the tangential stress is about 90 per cent of the yield strength. The average radial compressive stress through the wall for this reduction may be expressed as the product of the tangential stress and the ratio of the wall thickness of the tube to the mean diameter of the tube, so that for the dimensions of the present tubes it is about 4 per cent of the yield strength.

† This curve was calculated from stress-strain and sinking-stress data obtained from isotropic copper tube using the Siebel and Weber²² analysis as recently modified.²³ In the range of reduction and relative thickness of the tube employed here, the comparison of theoretical and experimental values is excellent.²³

approximate straight lines over the interval recorded within close enough limits to obtain a single value of slope for each line. These slopes may be compared with the data presented in Fig. 3, if either set of data could be reduced to the same form of presentation as the other. This can easily be done if it is remembered that the gauge axis in Fig. 3 is, for each curve, the $[001]$ axis and the width axis is normal to both the $[001]$ axis and the direction in which the tensile stress was applied. In the tube-sinking experiments the gauge axis is still the $[001]$ axis for both specimens,

whereas it is the drawing direction that is normal to both the $[001]$ axis and the direction in which the compressive stress was applied (tangential axis).

These curves were not, of course, obtained under a simple uniaxial compressive stress system, but under one that was contaminated with other stresses. If it is

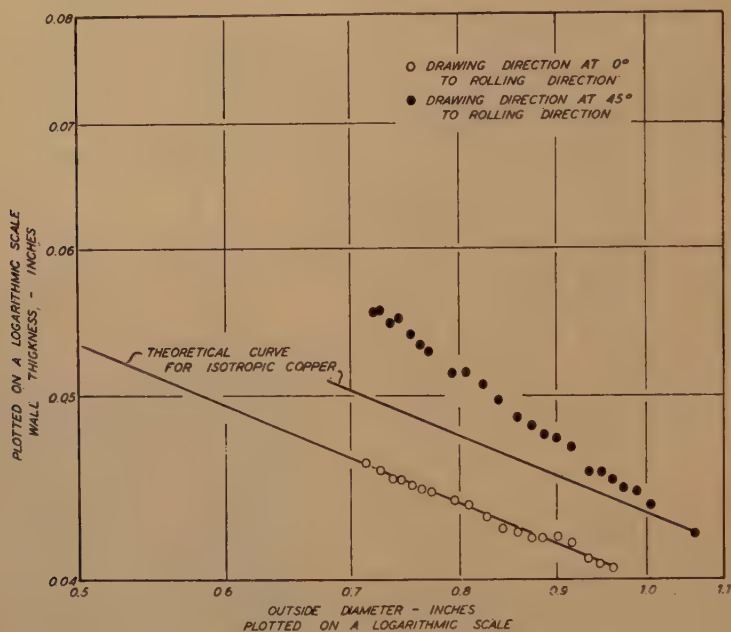


FIG. 7.—DIMENSIONAL CHANGES OF ARTIFICIAL TUBES SUNK SMALL AMOUNTS IN SUCCESSIVE PASSES.

Thus the slopes obtained from Fig. 7 that give the interdependence of hoop strain and thickness strain can be compared with the data in Fig. 3 if they are converted to a slope that gives the interdependence of thickness strain and strain in the drawing direction (longitudinal strain). This can be done by means of the basic equation

$$d \ln h + d \ln t + d \ln l = 0$$

where $\ln h$ = hoop strain,

$\ln t$ = thickness strain,

$\ln l$ = longitudinal strain.

Fig. 8, employing the same coordinates as Fig. 3, shows the curves obtained by this manipulation.

recalled from Fig. 7 that the sample tube formed from a strip cut at 0° to the rolling direction, behaved in the same manner that isotropic copper acts, it would appear quite likely that under a simple uniaxial compressive stress system a strip cut at 0° to the rolling direction, like isotropic copper, would expand equally in the width and gauge directions, as suggested by curve B in Fig. 8. The possibility, too, must be admitted that a specimen if cut from a strip and tested in compression at 45° to the rolling direction (with no tensile stresses acting along the width axis or compressive stresses acting along the gauge axis) would expand in the gauge direction more rapidly for a given expansion in the width direction than did the metal in the tube formed from

strip cut at 45° to the rolling direction. It is suggested that the curve *D* in Fig. 8 could describe the relative rates of deformation in this case.

with polar grids, which were used in measuring the strain suffered during the cupping operation. Measurements of radial and circumferential line segments were made

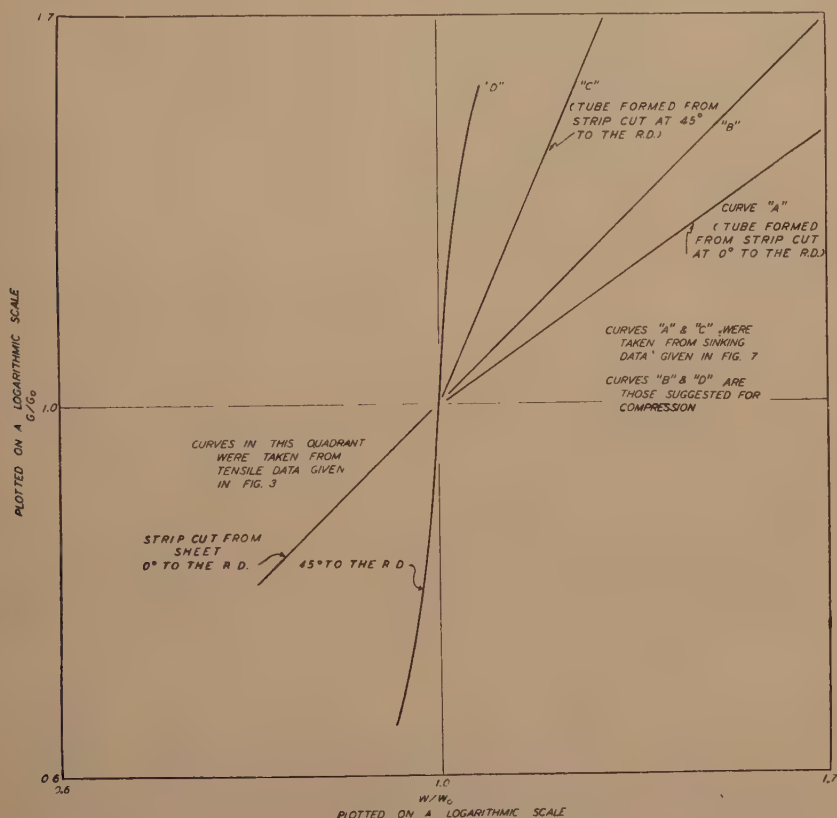


FIG. 8.—COMPARISON OF DATA OBTAINED FROM FIG. 7 WITH THAT OBTAINED FROM FIG. 3.

EVIDENCE OF DIRECTIONALITY IN DEFORMATION RATES IN THE THREE PRINCIPAL DIRECTIONS FOR THE STRESS SYSTEMS ENCOUNTERED IN PURE CUPPING

Cupping experiments were conducted on isotropic and 100 per cent cubically aligned copper using a $1\frac{1}{2}$ -in. diameter blank of 0.040-in. gauge. The punch diameter was 0.750 in. while the die diameter was 0.890 in. These diameters allowed ample clearance between punch and die to avoid ironing. The blanks were prepared

with a Brinell microscope while measurements of gauge were made with pointed-nose micrometers. The cupping of 100 per cent cubically aligned copper was interrupted at four stages in the process and strain measurements were made at each step.

The exact stress systems existing within the metal during a pure cupping operation (where no hold-down or ironing exists) can be generalized in the following manner.

Radial Stress.—Radial stress will pass from zero at the edge of the drawpiece to

some tensile value in the base of the cup. The exact function by which this stress passes from one end value to the other will

Thickness Stress.—Thickness stress will be small and may be neglected in the present study, though it may be stated

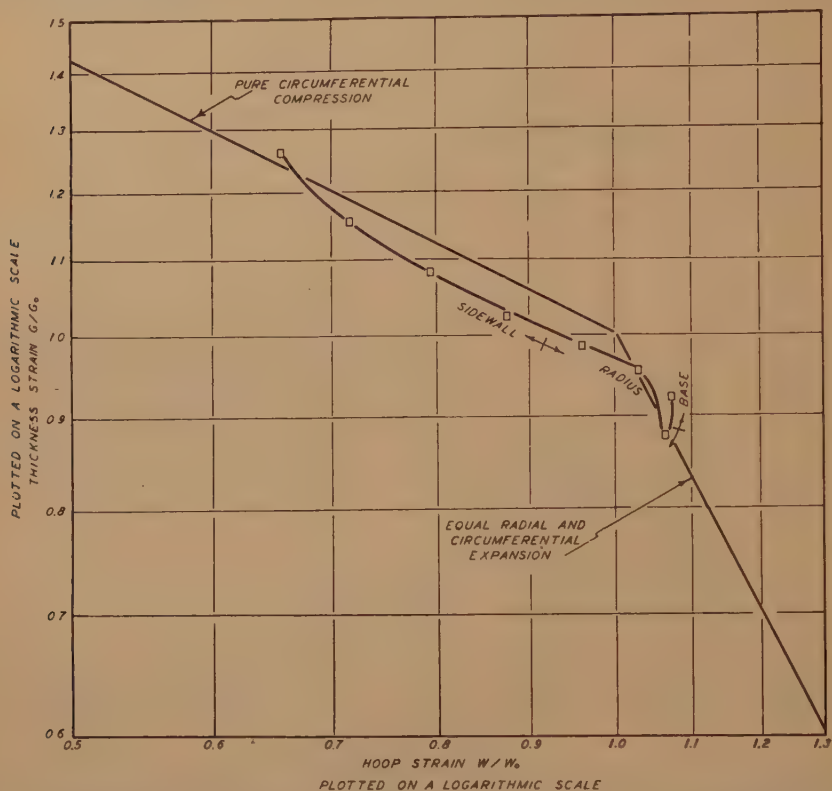


FIG. 9.—THICKNESS STRAIN PLOTTED AS FUNCTION OF HOOP STRAIN FOR PURE CUPPING OPERATION.

depend upon a host of press conditions (die contour and surface, punch contour and surface, lubrication, speed of drawing, etc., etc.) and the stage to which the cupping has progressed at any given moment.

Hoop Stress.—Hoop stress will pass from a compressive value, equal to the yield strength of the metal, at the edge of the drawpiece to a tensile value in the base approximately equal in magnitude to whatever radial stress exists there. The same remarks may be made regarding the exact path which this stress follows from the edge to the base of the cup as were made for the radial stress.

that it is generally compressive throughout the drawpiece.

Combination of Stresses

It is seen, therefore, that throughout the entire cupping process the edge of the drawpiece is subjected to a simple uniaxial compressive stress in the hoop direction and it is to be inferred, therefore, that for a given negative hoop strain, the radial and thickness strains will be positive and one half as large. Similarly, throughout the entire process the base of the drawpiece is subjected to approximately equal radial and hoop stresses and it is to be expected

that for a given positive hoop strain there will be an approximately equal positive radial strain while the thickness strain will be negative and about twice as great.

of gauge with no accompanying hoop strain (in the radius of the cup) or it suffers a thickening of gauge with an equal negative hoop strain and no radial deforma-

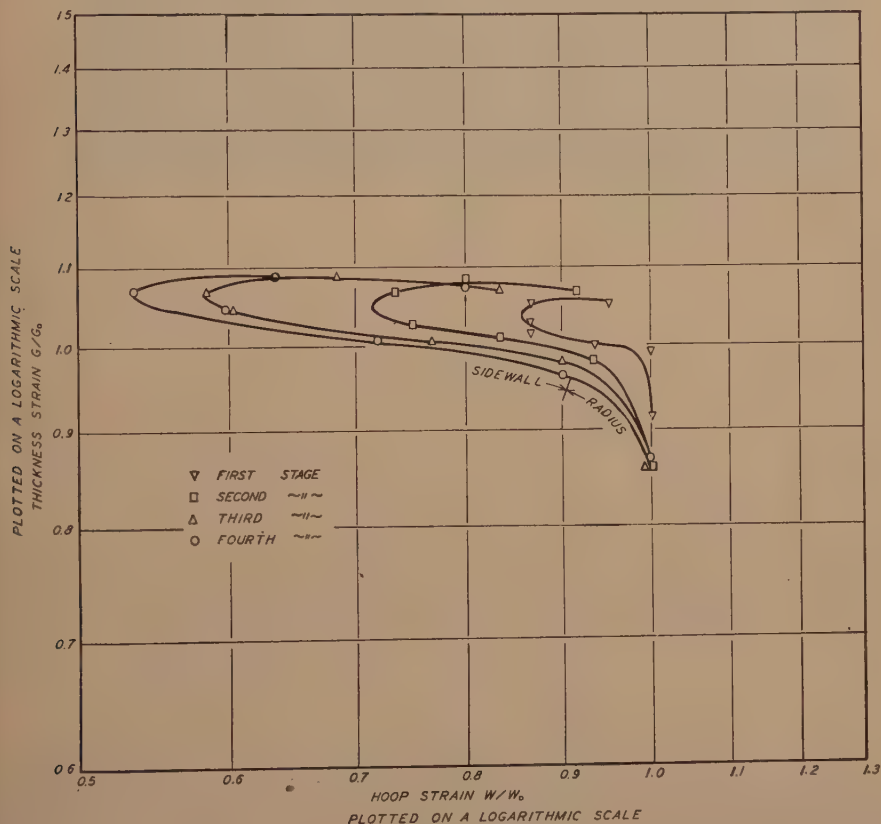


FIG. 10a.—THICKNESS STRAIN PLOTTED AS FUNCTION OF HOOP STRAIN FOR EAR CUP DRAWN FROM 100 PER CENT CUBICALLY ALIGNED COPPER. Four progressive stages of cupping operation are recorded.

These deformations are seen in Fig. 9 for a copper cup drawn from perfectly isotropic copper.

When 100 per cent cubically aligned copper is cupped without ironing or hold-down, the metal in the ear of the cup, while giving different shaped curves (Fig. 10a) still deforms over the same hoop strain-thickness strain ratios as isotropic copper. The metal in the trough of the cup on the other hand deforms in a unique way (Fig. 10b): either the metal undergoes a thinning

(in the wall of the cup). This is true for all four stages studied. This latter fact can be easily if uncritically demonstrated by measuring the radial length of a blank and of the trough section of cup drawn with a small radius from 100 per cent cubically aligned copper. The lengths are practically the same before and after cupping (Fig. 11).

The metal in the element lying at 45° to the rolling direction suffers the same external changes in dimensions (in all four

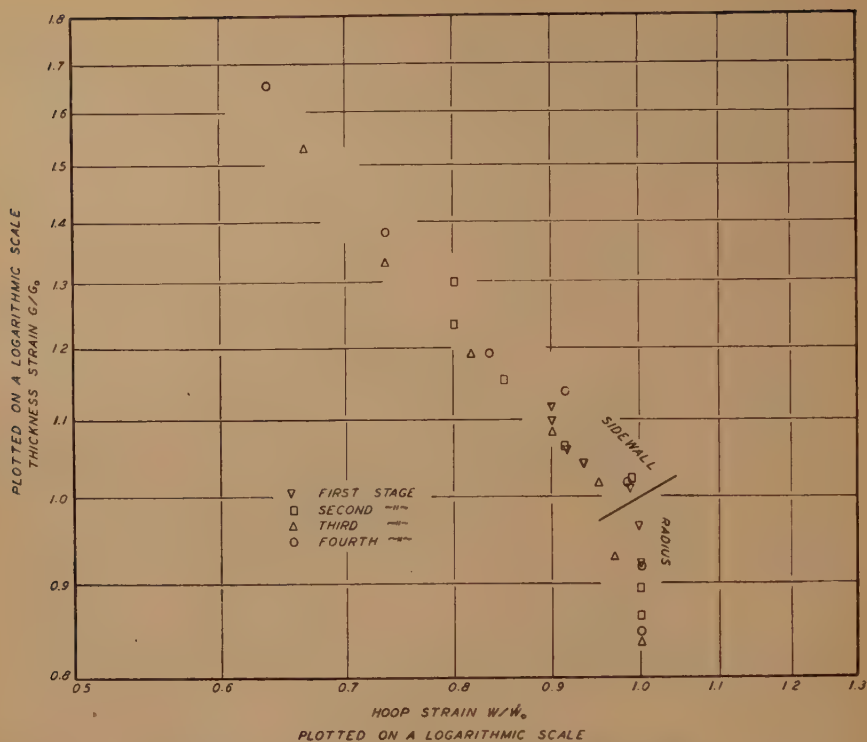
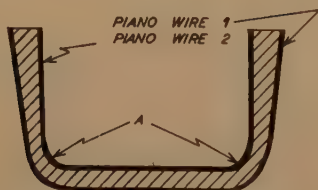


FIG. 10b.—SAME DATA AS IN FIG. 10a, FOR THE TROUGH.

LENGTH OF WIRE 1 = 1.60"
 — — — — — 2 = 1.43"
 AVERAGE = 1.515"
 BLANK DIAMETER = 1.500"



DIAMETRAL SECTION THRU TROUGH PORTION OF CUP.
 (SECTION TAKEN AS INDICATED
 IN UPPER RIGHT HAND PERSPECTIVE DRAWING)

FIG. 11.—ROUGH DEMONSTRATION OF FACT
 THAT TROUGH OF A CUP DRAWN FROM 100 PER
 CENT CUBICALLY ALIGNED COPPER DOES
 NOT ELONGATE SUBSTANTIALLY IN RADIAL
 DIRECTION.

What small increase in length is noted is
 due to thinning at the radii A-A.

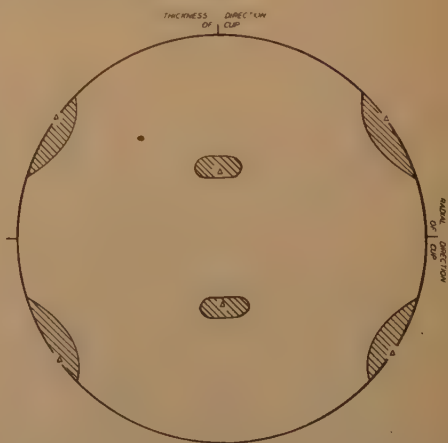


FIG. 12.—OCTAHEDRAL POLE FIGURE FOR
 LIP OF CUP AT 45° TO ROLLING DIRECTION
 (TROUGH).

Original orientation was $[001]$ axis parallel
 to thickness direction of cup $[110]$ axis parallel
 to radial direction of cup and $[1\bar{1}0]$ axis parallel
 to tangential direction of cup (normal axis of
 pole figure). Triangles indicate starting
 orientation.



FIG. 13.—DRAWPIECE: (a) NO LONGER HAS CIRCULAR OUTLINE; (b) ALREADY THICKENED IN TROUGH.

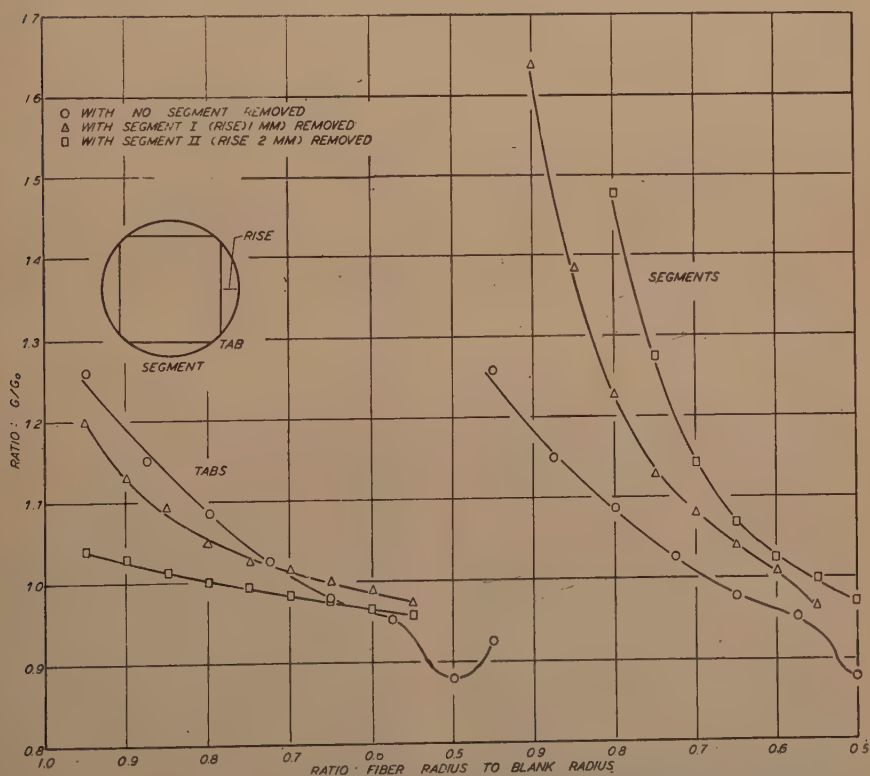


FIG. 14a.—EFFECT OF CUTTING SEGMENTS FROM BLANKS OF ISOTROPIC COPPER. Thickness strain as function of fiber radius. Ratio of radius of fiber in blank before cupping to radius of edge of blank is used as abscissa.

stages of the cupping process that were studied) as any metal that is cold-rolled; i.e., it has elongated in one direction (the gauge direction) and has been compressed

ize the mode of deformation encountered during cupping, synthesizing it from the data presented for tensile and compression tests. There are, however, a number of

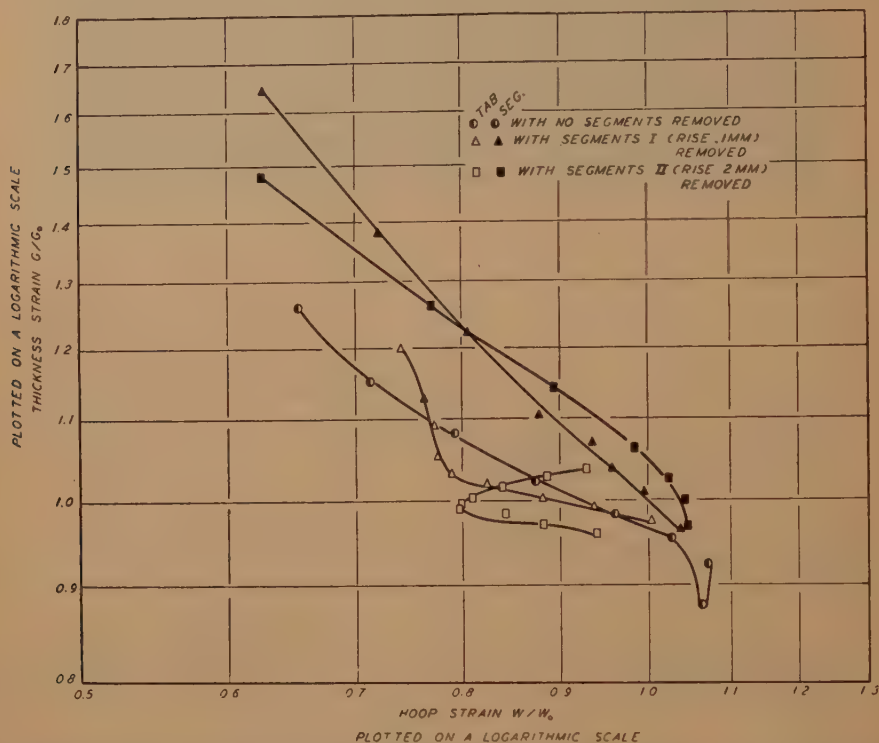


FIG. 14b.—SEE LEGEND FOR FIG. 14a.

Thickness strain as function of hoop strain. In latter graph, compare curve with circular symbols with Fig. 9 and curves with square symbols with Fig. 10.

in another direction normal to the first (the tangential direction) while suffering little or no deformation in a third direction normal to the first two (the radial direction). X-ray analysis of the element at 45° to the rolling direction after cupping produced the pole figure shown in Fig. 12. It is quite apparent that the pole figure has been produced by a simple rotation of the octahedral poles about the normal $[110]$ axis. A similar pole figure and rotation have been noted by Brick²⁵ for a single crystal of brass rolled from an original $(110)[001]$ orientation.

There is a strong temptation to rational-

complexities to the cupping process which make so simplified a rationalization hazardous. Some idea of these complexities may be gained from Fig. 13—a photograph of a partially formed cup—the metal is soft copper with a completely cubically aligned recrystallization texture—in which it is at once apparent that ears have already begun to form. The drawpiece when viewed from above no longer has a circular outline—in fact, it tends toward a square.* A close inspection of the cup wall reveals

* See photographs of partially drawn cupronickel cups (Bassett and Bradley²⁶) and brass cups (Palmer and Smith¹⁷).

that it is much thicker in the sector containing the trough than it is in the sector containing the ear.* These dimensional changes are evidences of directionality in

restricted number of crystallographic slip systems may be operative and which, therefore, may be differently sensitive—or even insensitive—to the deviations

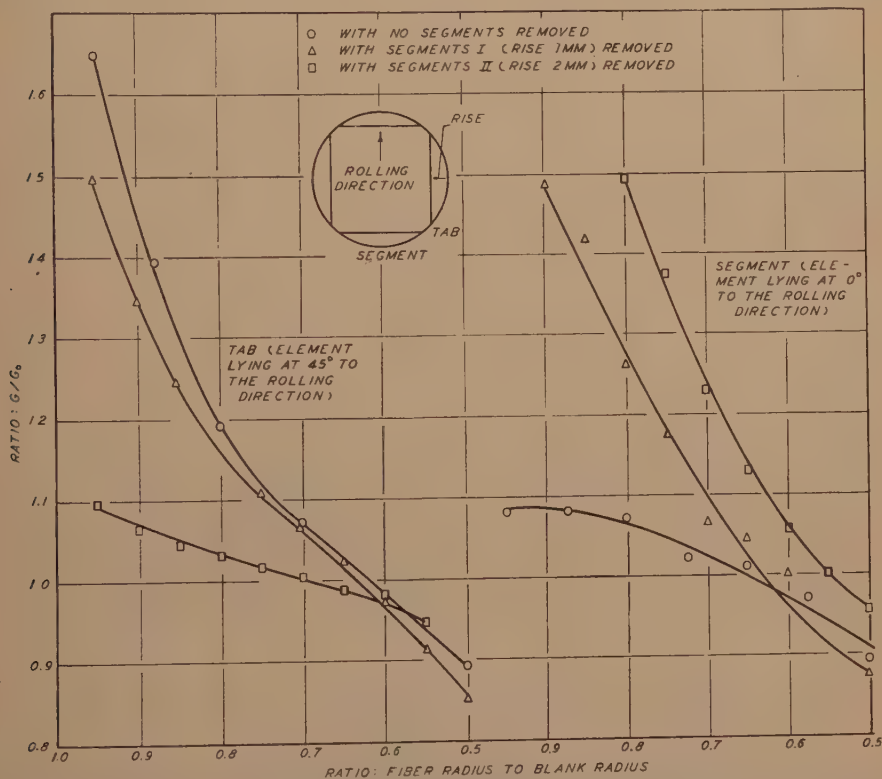


FIG. 15a.—EFFECT OF CUTTING SEGMENTS AT 0° AND 90° TO ROLLING DIRECTION FROM BLANKS OF ANISOTROPIC COPPER.

Thickness strains as function of fiber radius. Ratio of radius of fiber in blank before cupping to radius of edge of blank is used as abscissa.

triaxial deformation rates, but in themselves alter the stress system acting within the metal during the cupping operation.

The effect of these many factors on the earing tendency of metal can be studied easily by artificially producing them separately in metal that under normal condition would produce no ears. It is a moot point, however, whether the experience obtained from these studies could be applied to anisotropic metal in which a

engendered in the stress system. For a full and proper understanding of the effect of these secondary factors, it is therefore necessary to study their effect when artificially produced in both directional and nondirectional metal.

For example, "squared" blanks were prepared by shearing off four segments of circular blanks of (1) copper strip that gave no ears when drawn from a circular blank and (2) 100 per cent cubically aligned soft copper strip, which gave ears at 0° and 90° to the rolling direction when

* See graphs in Swift.²⁴

drawn from a circular blank. In the latter case the blanks were sheared so as to leave the corners of the square (1) at 0° and 90° to the rolling direction (2) at 45°

tropic copper (Fig. 9) to those characteristic of cups drawn from round blanks of 100 per cent cubically aligned copper (Fig. 14b).

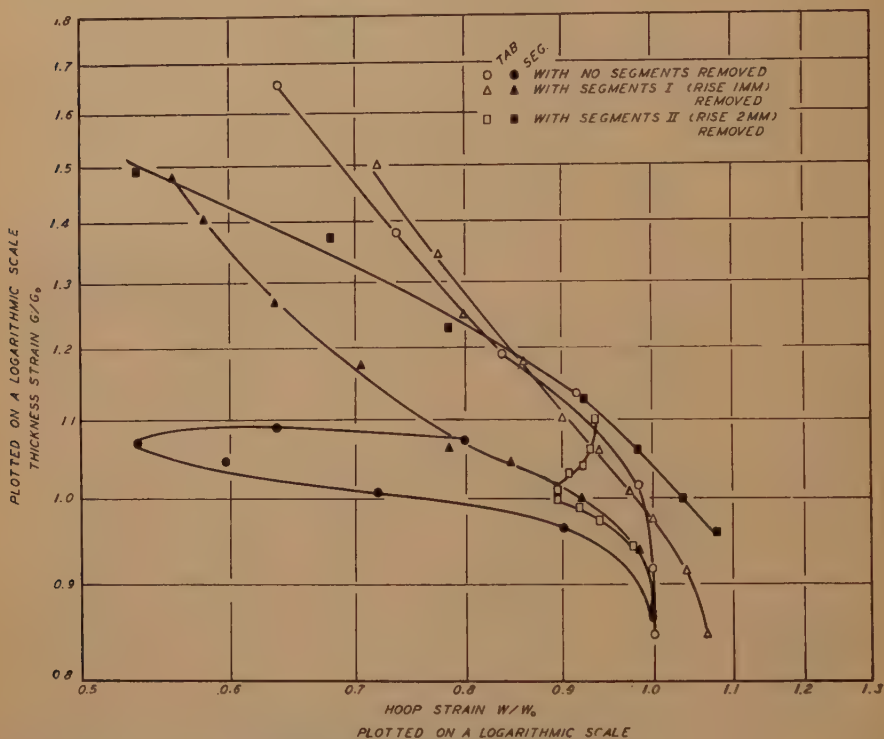


FIG. 15b.—SEE LEGEND FOR FIG. 15a.
Thickness strains as function of hoop strain

to the rolling direction. Two sets of experiments were performed, one in which the rise of the segment was 1 mm., the other in which the rise was 2 mm. The blank diameter and other cupping conditions were the same as described above.

The cups drawn from isotropic copper have thickened in gauge at a greater rate in the direction of the segment than in the direction of the tab (Fig. 14a). Further, the relative rates (as the segments are cut deeper) of hoop and thickness strains progressively pass from that typical of cups drawn from round blanks of iso-

The cups drawn from 100 per cent cubically aligned copper can be radically affected by cutting segments from the blanks. For instance, in the cups drawn from blanks sheared in such a way as to leave the tabs at 45° to the rolling direction, the gauge thickens in the element lying at 0° to the rolling direction as the segment is cut deeper while at the same time the gauge thins out in the element lying at 45° to the rolling direction (Fig. 15a). The relative rates of deformation likewise are altered (Fig. 15b). The changes effected by cutting segments from 100 per cent

cubically aligned copper blanks so as to leave tabs at 0° and 90° to the rolling direction are less spectacular (Fig 16).*

metal, but also is sensitive to the stress system engendered in the drawpiece itself.

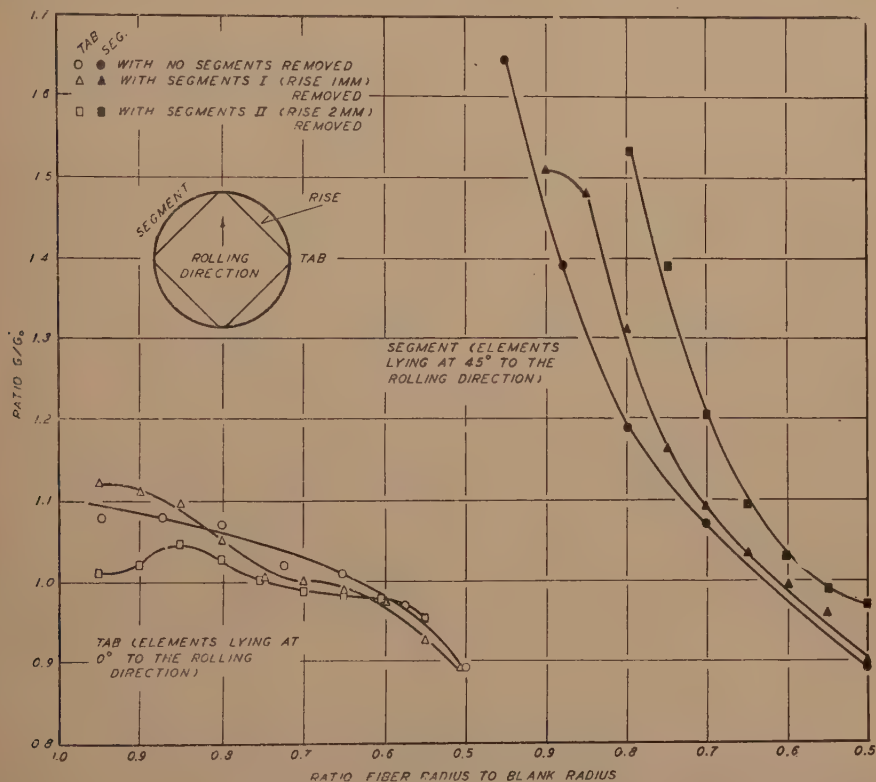


FIG. 16a.—EFFECT OF CUTTING SEGMENTS AT 45° TO ROLLING DIRECTION FROM BLANKS OF ANISOTROPIC COPPER.

Thickness strain as function of fiber radius. Ratio of radius of fiber in blank before cupping to radius of edge of blank is used as abscissa.

It must be concluded, therefore, that the mode of deformation occurring during the cupping of anisotropic copper is not only a function of the crystallography of the

CORRELATION OF RELATIVE TRIAXIAL DEFORMATION RATES DETERMINED IN TENSILE TEST WITH MICROSTRUCTURE OF SOFT COPPER

* One detail in this case is of interest, however. The element lying at the very top of the ear of a cup drawn from a circular blank of 100 per cent cubically aligned copper is not as severely deformed as an element lying half way down the side wall in the ear (see Fig. 10a). The tendency has been so exaggerated by cutting tabs at 0° and 90° to the rolling direction that for a 2-mm. deep segment the element at the very tip of the tab is hardly deformed at all! This may be seen in Fig. 16b, where the last point of the curve lies quite close to unity on both the ordinate and abscissa.

From the exploratory work, it appears that entirely new fields of research must be exhaustively studied before a clearer understanding of the phenomenon of earing during cupping can be had. In this, the second part of the present paper, the directionality of deformation rates in the three principal directions of copper de-

formed in simple tension is correlated with the microstructure of the metal and the rolling schedule by which the metal

tions of the following variables were represented: ready to finish anneals—900°F. and 1200°F.; final reductions—8, 12, 16,

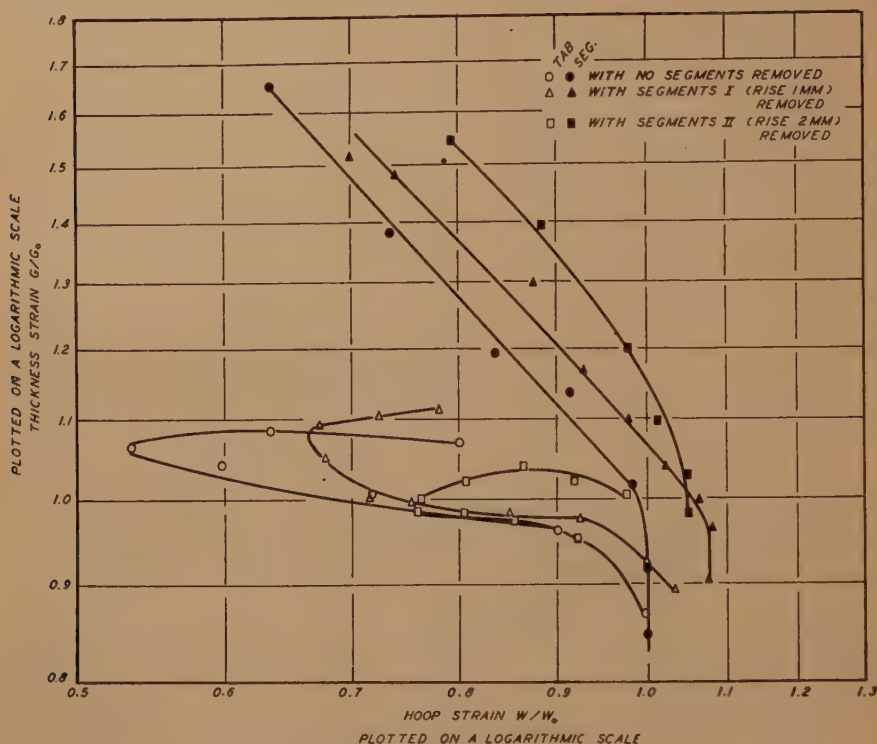


FIG. 16b.—SEE LEGEND FOR FIG. 16a.
Thickness strain as function of hoop strain.

was produced. Further, a study of earing conditions is correlated with the rolling schedule.

EXPERIMENTAL PROCEDURE

Material Employed

The copper strip was processed so as to include all possible earing conditions known. An attempt was made, moreover, to investigate those conditions in strip in which preferred orientation is indistinct or undeveloped—as well as those cases where preferred orientation is pronounced.

Strip intended to give ears at 0° and 90° to the rolling direction in various intensities was produced by processing copper in such a manner that all possible combina-

20 and 28 B. and S. gauge numbers; final anneals —900° and 1200°F.

Strips intended to give ears at 45° to the rolling direction were prepared in two different ways: (1) by rolling 86 per cent, annealing at 1650°F., rolling 80 per cent and annealing at 1500°F.,^{27,28} (2) by rolling 25 per cent from a complete cubically aligned strip and annealing.^{18,29}

All break-down reductions were four B. and S. gauge numbers and all break-down anneals were 1200°F. The final gauge for all strips was 0.040 inch.

METHODS OF TESTING

Samples were examined microscopically (after final annealing), and the per-

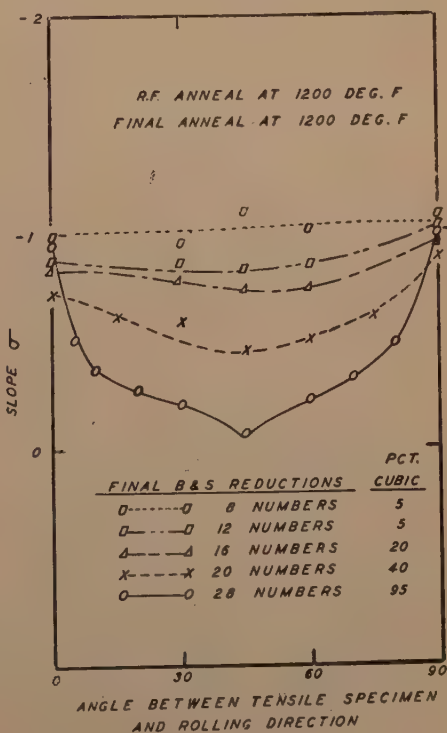
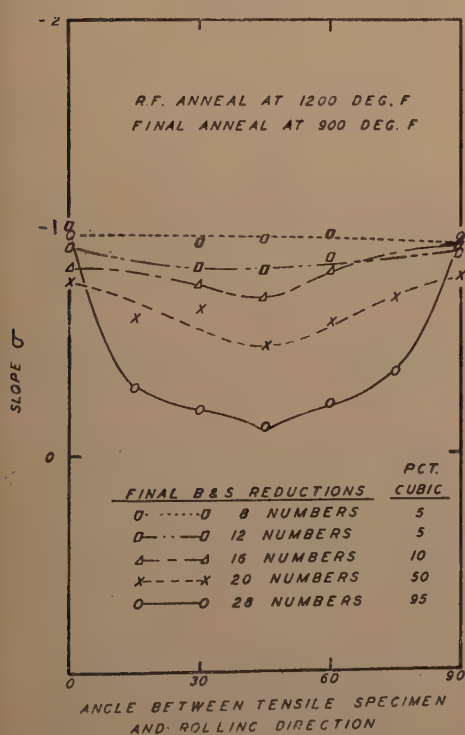
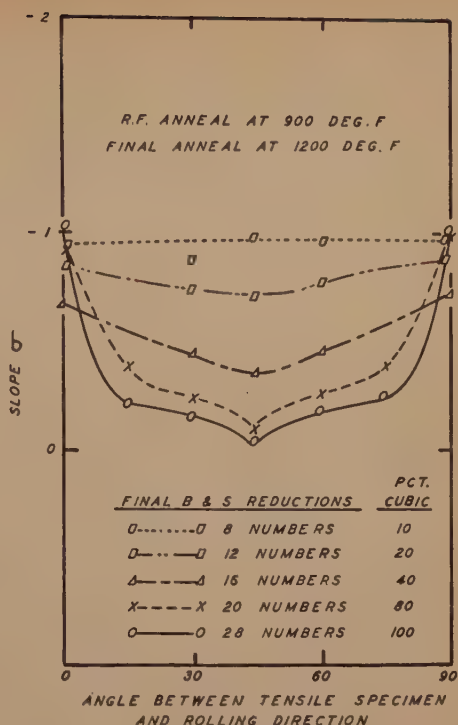
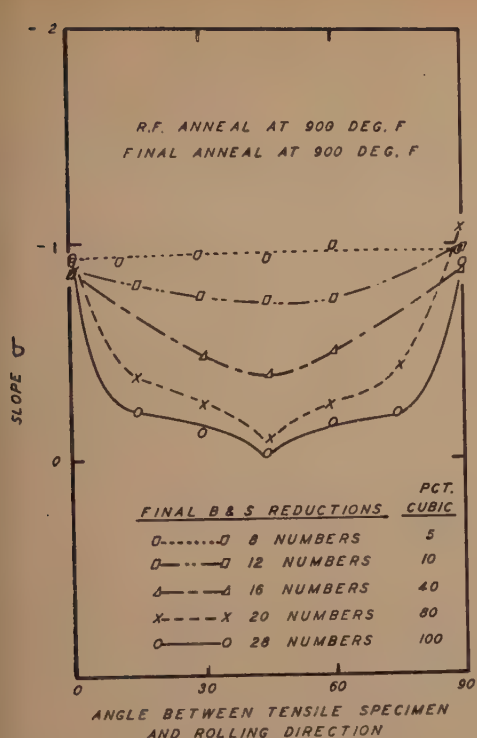


FIG. 17.—VARIATION OF SLOPE σ WITH ANGLE TO ROLLING DIRECTION FOR COPPER STRIPS ROLLED AND ANNEALED ACCORDING TO SCHEDULES NOTED.

centage of cubically aligned grains was recorded.¹⁸

Tensile specimens were milled from strip at various angles to the rolling direction

and a die that yielded a final cup wall equal to the original blank thickness. The angle of the ears, with respect to the rolling direction of the strip for each cup, was

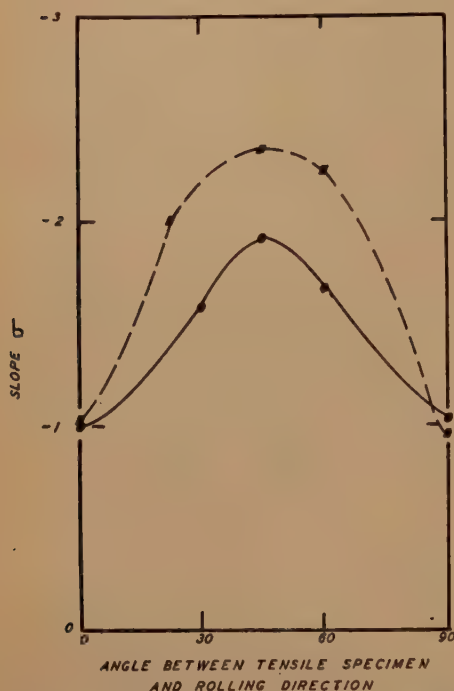


FIG. 18.—SLOPE σ VALUES FOR COPPER STRIPS YIELDING EARS AT 45° TO ROLLING DIRECTION.

Material of lower curve rolled 86 per cent, annealed 1650°F. , rolled 80 per cent to 0.040 inch, annealed 1500°F. ²⁷

Material of upper curve rolled 25 per cent, from 100 per cent cubically aligned stock, annealed 1000°F. ¹⁸

and tested in the manner described in Fig. 2. The values of unit width and unit gauge were plotted on logarithmic scales. The slopes of these curves, taken from the origin, were then plotted as $\frac{d \ln w/w_0}{d \ln g/g_0}$ (hereafter referred to simply as σ) as a function of the angle between the rolling direction and the tensile specimen.

Cupping tests were carried out in which $1\frac{1}{2}$ -in. diameter blanks were cupped with no hold-down plate, using a $\frac{3}{4}$ -in. punch

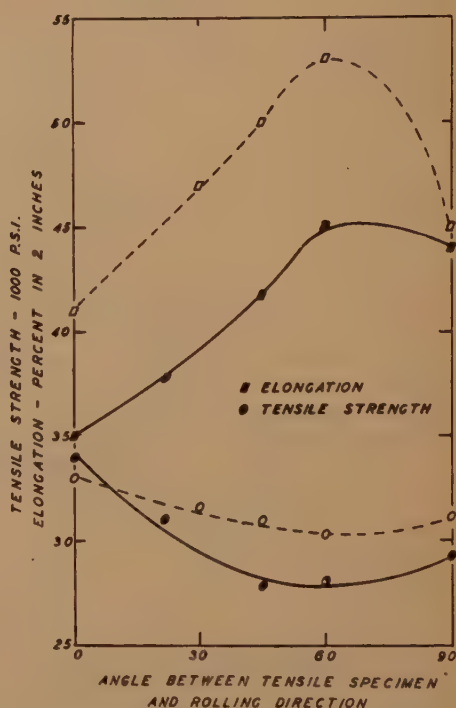


FIG. 19.—SIMILARITY OF DIRECTIONALITY OF TENSILE STRENGTH AND PERCENTAGE OF ELONGATION FOR TWO COPPER STRIPS YIELDING EARS AT DIFFERENT ANGLES TO ROLLING DIRECTION.

Ears at 45° to R.D.: closed symbols rolled 25 per cent from 100 per cent. Cubically aligned stock annealed 1000°F. ¹⁸

Ears at 0° and 90° to R.D.: open symbols annealed 900°F. , rolled 16 B. and S. numbers, annealed 1200°F.

recorded. The percentage of ear height differs fundamentally from the conventional "per cent ear height," in that the datum plane used for all measurements is the base of the side wall and not the base of the cup.

RESULTS

The directionality of σ for the copper strips that gave ears at 0° and 90° to the

rolling direction is given in Figs. 17a through 17d, and for the copper strips that gave ears at 45° to the rolling direction in Fig. 18. An interesting point to be

both strips, yet in one case ears were developed at 45° to the rolling direction and in the other at 0° and 90° to the rolling direction.

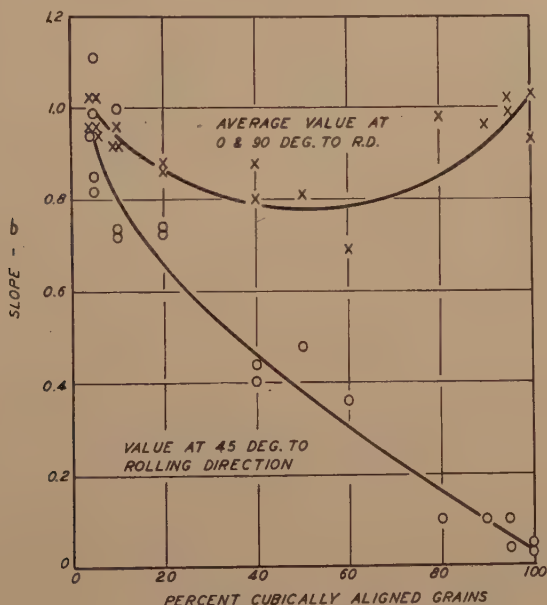


FIG. 20.—VARIATION OF SLOPE σ AT 0°, 90° AND 45° TO ROLLING DIRECTION AS FUNCTION OF PERCENTAGE CUBICALLY ALIGNED GRAINS IN MICROSTRUCTURE OF COPPER STRIPS INVESTIGATED.

noted is that in the coppers studied the values of σ are a maximum at 0° and 90° for the strips that eared at 0° and 90° (Figs. 17a through 17d) and likewise are a maximum at 45° for strip with ears at 45° (Fig. 18).

These results indicate that there is no known case to be encountered in soft copper strip where a qualitative prediction of the position of the ears cannot be made. This correlation becomes all the more significant in considering the specimen rolled 25 per cent from a completely cubically aligned structure and the strip given the following treatment: ready-to-finish anneal 900°F., final reduction 84 per cent, final anneal 1200°F. The directionality of tensile strength and elongation for these two strips are given in Fig. 19. The distribution of both properties is roughly parallel for

In Fig. 20, the average values of σ at 0° and 90° and the value of σ at 45° to the rolling direction (taken from Fig. 17) are plotted as a function of the percentage of cubic alignment existing within the sample. The behavior of the curve for the average value of σ at 0° and 90° is worthy of comment. It will be noticed that the curve drops from a value of one at 0 per cent cubic alignment to a value of about 0.8 at 50 per cent cubic alignment and then rises once more to one at 100 per cent cubic alignment. It is suggested that a second orientation occurs in sufficient intensity at about 50 per cent cubic alignment to cause this minimum in the curve.

The difference in the average value of σ at 0° and 90° and the value of σ at 45° to the rolling direction varies with the severity of final reduction, as shown in Figs. 21a

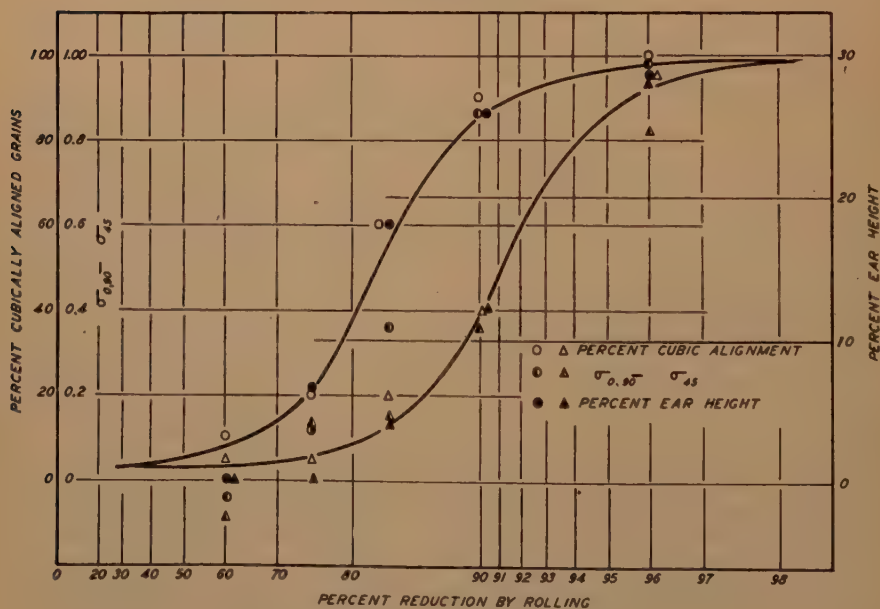
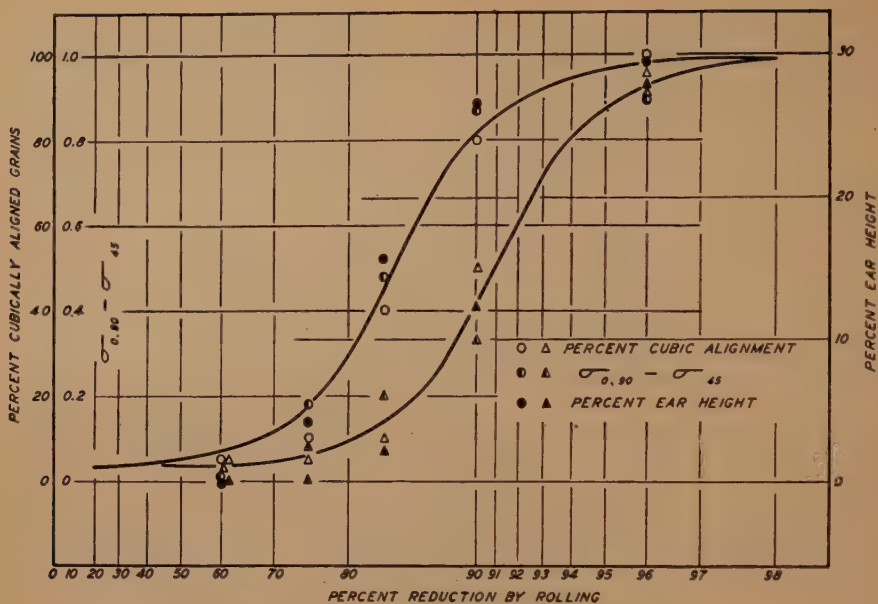


FIG. 21.—PLOT OF THREE QUANTITIES.

1. Percentage of cubic alignment in microstructure.

2. Difference between σ at 0° , 90° and σ at 45° .

3. Percentage of ear height on drawn cups as a function of final reduction.

(a) 900°F . Final anneal.○ Ready-to-finish anneal. 900°F .△ Ready-to-finish anneal. 1200°F .(b) 1200°F . Final anneal.○ Ready-to-finish anneal. 900°F .△ Ready-to-finish anneal. 1200°F .

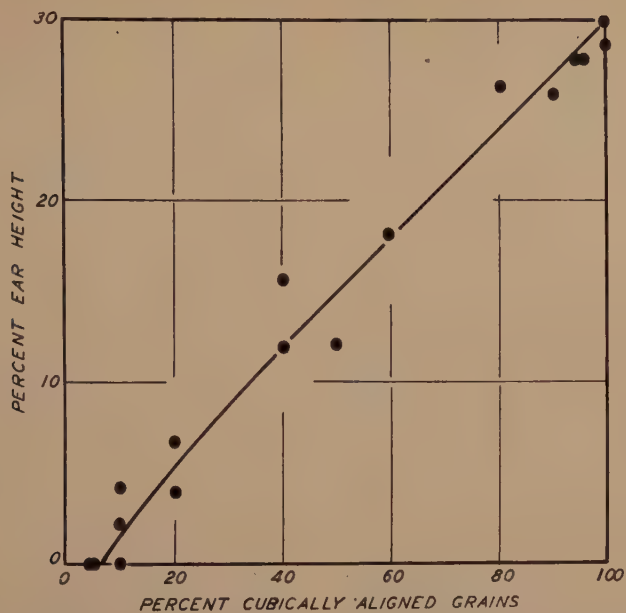


FIG. 22a.—RELATIONSHIP BETWEEN PERCENTAGE EAR HEIGHT IN DRAWN CUP AND PERCENTAGE CUBIC ALIGNMENT IN MICROSTRUCTURE.

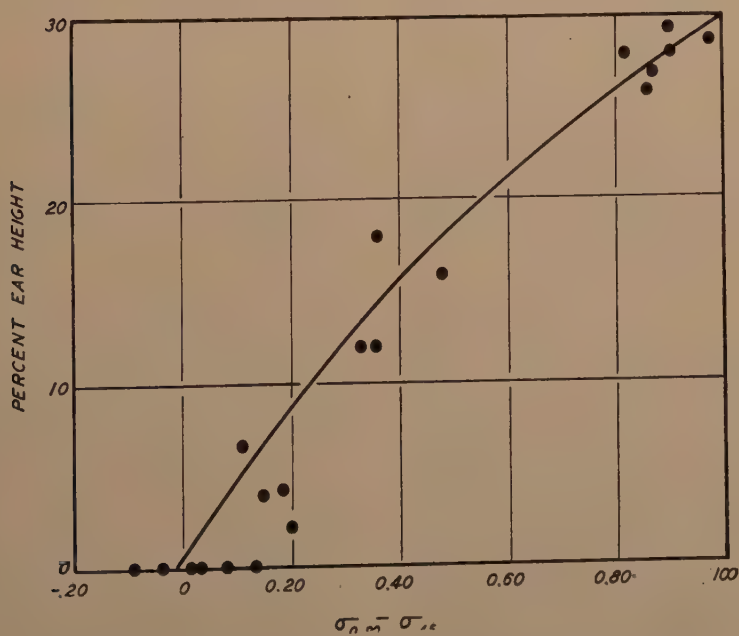


FIG. 22b.—RELATIONSHIP BETWEEN PERCENTAGE EAR HEIGHT IN DRAWN CUP AND DIFFERENCE BETWEEN VALUES OF σ AT 0° , 90° AND σ AT 45° TO ROLLING DIRECTION.

and b . In these same graphs the percentage of cubically aligned grains is plotted. There is a rough parallelism between the two functions. It should be noted, however, that at relatively low reduction values the cubic alignment does not drop below 5 per cent (for reasons of probability) while values of $(\sigma_{0^\circ, 90^\circ} - \sigma_{45^\circ})$ can and do go to zero and below. There is also a rough parallelism of percentage of ear height when plotted against the final reduction with these two functions (Figs. 21a and 21b). Because of the similarity of these three functions there is the obvious suggestion that a straight line or near straight line relationship can be empirically made between any two of the three. This has been done in Figs. 22a and 22b. These are empirical relationships for many reasons:

1. The parallelism of the three functions when plotted against the final reduction is coincidental. It has just been pointed out, for example, that the values of σ are probably affected by a second orientation, no account of which is made on Fig. 22a.

2. The percentage of ear height is the product of an entirely different stress system from that existing in tensile testing and is controlled by certain conditions of continuity and compatibility occurring in the drawpiece being cupped. These factors are completely ignored in the representation made in Fig. 22b.

SUMMARY

1. Attention is diverted from a correlation of directionality in rupture properties (tensile strength and elongation) with the earing tendency of metal and drawn to the possibility of a correlation of directionality in flow properties (relative rates of deformations in three principal directions) with the earing tendency of metal.

2. Extreme variation in the relative rates of deformation in the three principal

directions is found when specimens of 100 per cent cubically aligned copper are pulled in simple tension at various angles to the rolling direction.

3. Similar variation is found when 100 per cent cubically aligned copper is tested under a stress system approaching simple compression.

4. The relative rates of deformation of isotropic and anisotropic copper were studied in a pure cupping operation (with no ironing and no hold-down).

5. The effect of different shaped blanks on the relative rates of deformation of isotropic and anisotropic copper was reported.

6. A correlation has been made between the microstructure of soft copper strip and triaxial deformation rates as determined in a simple tension test.

7. A detailed study of all known earing conditions of soft copper strip has led to a means of determining the position of ears from the shape of curves in which σ is plotted as a function of the angle to the rolling direction.

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DISCUSSION

(Gerald Edmunds presiding)

F. H. WILSON.*—Our friends from the Chase Brass and Copper Co. in Cleveland have a capacity for getting a great deal of experimental work and a lot of data into a very condensed form, and it takes a lot of study to ferret out all that is there.

To those of us who have spent some time in puzzling over the mechanism of ear formation, the new line of attack presented in this excellent paper is particularly interesting. The complexities of the question are more clearly resolved and the nice correlation between the rates of triaxial deformation and earing behavior the authors have found for anisotropic copper, regardless of whether ears are at 45° or at 90° , is very gratifying.

These comments may refer to what the authors have considered to be obviously implied by the experimental data and, if so, it still might be just as well to get it down on paper for the benefit of those who, like me, have to think out loud for clarification.

It seems to me that the statement in the paper that "It must be concluded, therefore, that the mode of deformation occurring during the cupping of anisotropic copper is . . . sensitive to the stress system engendered in the drawpiece itself," can be amplified. The triaxial stress system is described as radial tension, circumferential or hoop compression, and thickness compression. The general pattern of earing behavior, as described,

becomes a little clearer when we take at least part of this stress system and follow its influence on triaxial strain.

Radial tensile stresses increase from zero at the edge of the drawpiece to a maximum at the radius. Referring to deformation in the ear direction as seen in Fig. 1, there is considerable less radial and hoop strain at the rim than in the sections below the rim (as pointed out in a footnote to the paper). The crystal orientation is the same and the compressive hoop stresses are less away from the rim. Thus, in spite of lesser compressive hoop stress at the lower section, there seems to be greater hoop strain. Do the authors agree that the difference in strain between these two elements is due to the increasing radial tensile stress? Accompanying the change in strain in radial and circumferential directions, there is less decrease in thickness strain (from rim to radius) than occurs for isotropic copper, making the curve in Fig. 10a almost horizontal at the top of the hook.

When the effect of cutting segments is examined, the assumption, which I believe valid, that there is greater radial tensile stress in the tab direction than in the segment direction, helps in interpretation of the curves. For isotropic copper, the decrease in thickness strain from edge to radius in the tab direction becomes less marked as the segments are removed, the tendency toward thickening under hoop stress being counteracted by the higher radial tensile stress in the tab direction (Fig. 14a). (The absence of metal at the segment must also alter the compressive hoop stresses.) When tabs are at 45° for anisotropic copper, the radial tensile stress in the tabs counteracts the crystallographic tendency to thicken. This can be seen in Fig. 15a. When the tabs are at 0° and 90° (Fig. 16a) the radial tensile stress augments the crystallographic tendency toward low thickness strains and, as pointed out in the footnote to the paper, thickness strain is practically eliminated when 2-mm. segments are removed.

I would like also to ask about one other point. Coppers from two different rolling and annealing schedules giving ears at 45° are described in the paper. The authors also show an anisotropic copper that has maximum elongation and minimum tensile strength at about 60° , and yet gives ears at 0° and 90° . Can the

* American Brass Co., Waterbury, Connecticut.

authors give some idea of the textures to be found in these strips?

GERALD EDMUNDS.*—My discussion is in reference to Fig. 20, which presents data on the variation of the slope sigma as a function of the percentage of cubically aligned grains in copper strips. (The slope sigma is a function of the relative change of width to thickness of strip specimens in tension testing.)

In a randomly oriented metal, and in one oriented 100 per cent cubically, fourfold symmetry exists about the rolling direction and the transverse direction; hence, the slope sigma would be expected to have the value 1.0, as reported by the authors. The textures when incompletely developed by cold-rolling, however, would be expected to have only twofold symmetry about these axes, therefore the slope sigma would be expected to depart from unity. The shape change undergone by the metal in rolling should tend to cause cube planes to approach parallelism with the rolling surface more rapidly than they approach parallelism with the plane including the surface normal and the rolling direction. Thus it is not surprising that the change in slope sigma is a decrease, corresponding to the thickness decreasing more than the width in the tensile test.

Thus there seems to be no need to postulate the origin of a second orientation to cause the minimum in the curve, Fig. 20. Actually the datum points are too few and too irregular to establish the location of the minimum, and the lowest actual value recorded by the authors lies at the 60 per cent abscissa value.

Regarding the 45° values, there is fourfold symmetry about the principal axes normal to the direction of elongation in the randomly oriented metal, but the symmetry is only twofold in the completely cubically oriented metal, hence the limiting cases need not have the same value. Of course, the direction of test makes no difference in the randomly oriented metal (here sigma should always be unity). In the completely cubically oriented metal the octahedral planes that could account for narrowing of the specimen are all inactive, being parallel to the direction of elongation, while the ones that could account for thinning

of the specimen are very favorably oriented for slip, 35° from the direction of elongation. Thus the decrease of σ from 1.0 to zero as the orientation texture changes from random to 100 per cent cubical alignment is rational.

I should like to know whether the copper strip reduced eight numbers and then annealed (Fig. 17) developed ears.

J. T. NORTON.*—Would it be at all helpful in this problem to be able to measure the actual stresses in the material during the course of deformation; that is, to know what the stresses are not only in the elastic region but also after the material has undergone considerable plastic deformation?

I ask that question because I think we are now in a position to measure such stresses by means of X-ray diffraction, not only in the elastic range but also after the material has been plastically deformed. Another thing we can do after the material has been deformed is to determine the residual stresses that exist in the part; that is, compare the residual stresses in the part that has been subjected to large deformation as compared with the regions where the deformation has been somewhat less.

We can determine also the distribution of stresses below the surface—that is, the stress through the thickness of the material—and I should like to ask the various people who have discussed this paper whether that information would be of any value.

This method is still in a developmental state and I am not sure how well it can be applied to copper, but I know that it can be applied to other materials, and perhaps it might contribute to the solution of this general problem.

T. S. HOWALD (author's reply).—In answer to Professor Norton's question I would say: Yes, it would be very helpful. It would remove a lot of the supposition that we have been working on.

In reply to Mr. Edmunds' discussion, we should like to mention that secondary orientations have been noticed by Cook and Richards³⁰

* Massachusetts Institute of Technology, Cambridge, Massachusetts.

³⁰ Figs. 14 and 15 of ref. 29. See also ref. 18, Fig. 6a.

* American Brake Shoe Co., Mahwah, New Jersey.

in cold-rolled and annealed copper. The present authors have not found the second orientation to be quite so pronounced as Cook and Richards' Figs. 14 and 15 and as the discussion on page 219 of their paper would indicate. This discrepancy may be due to slightly different compositions in the two coppers investigated. In any event, there are indications of a second orientation from a metallographic basis. Whether this second orientation is responsible for the change in slope σ shown in Fig. 20 of the present paper, or whether this change is caused by the factors outlined in Mr. Edmunds' discussion, the authors are not prepared to say.

It would seem, however, from the micrographs and X-ray photograms given in Cook and Richards' paper, that for the microstructures representing 40 to 60 per cent cubic alignment (at which values the minimum in σ 0° to 90° and σ 45° occurs according to Fig. 20 in the present paper) the divergence of the cube planes from the plane including the surface normal and the rolling direction is of the same order as that of the cube planes from the rolling surface, although it must be admitted that the data do not permit any exact quantitative statements.

Figs. 21a and b indicate that copper rolled eight numbers (60 per cent reduction by rolling) produces nonearing strip for the ready to finish anneals employed in this investigation.

GERALD EDMUNDS.—I did not wish to imply that I did not think a second orientation did exist. I merely wanted to point out that my thought on it was that it was not necessary that there be a second orientation in order to develop the type of curve that was shown in Fig. 20.

T. S. HOWALD.—We do not think a second orientation is really necessary.

R. M. BRICK.*—Since people have told me that they did not understand the pole figures that I have made in the past, so I might tell the authors that I studied their figures of hoop thickness versus hoop strain, and I am sure that I had as much trouble.

Beyond that, I should like to ask whether they have had time to apply their analysis to

materials other than copper? I have always been curious about the fact that when approximately 5 to 7 per cent zinc is added to copper, the response of copper to an annealing operation is completely altered. The usual analysis of cupping has failed completely to account for the difference in behavior of copper and brass. I wondered whether the sigma analysis would take care of that?

T. S. HOWALD.—We have applied this method of determining the rates to various other metals. We have worked with 70-30 brass, and we have found that slope sigma values were a maximum at 45° for cups that produce four ears at 45° to the rolling direction. We found quite erratic results for the conditions under which six ears are produced.

We also applied this to two other metals in an exploratory manner; that is, we had some aluminum handy; I think it was 52S. We rolled it quite severely and annealed it and drew it into cups producing ears at 0 and 90°. Sigma values were a maximum at 0° and 90° also.

Likewise, we rolled some strip nickel rather heavily and annealed it. On cupping, it gave ears at 45° to the rolling direction, and the slope sigma values were again a maximum at 45°.

W. M. BALDWIN, JR., T. S. HOWALD and A. W. ROSS (authors' reply).—We should like to make a few precautionary remarks with regard to Dr. Wilson's discussion. In his fourth paragraph, Dr. Wilson has summarized the generalized description of stresses acting in a cupping operation given on pages 100 and 101 and has applied this summary in his fifth paragraph to a discussion of the strains encountered in metal that ears. This should not be done, properly speaking. As stated on page 99, directional metal introduces many complications which "alter the stress system acting within the metal during the cupping operation." This alteration may be quite radical. Recent studies made in Cleveland show that nondirectional metal blanks prepared with tabs and segments as described in the paper actually display *radial compression* instead of radial tension in the direction of the segment! This work is being continued and it is hoped more quantitative data can be reported at some later date. Until such time,

* University of Pennsylvania, Philadelphia, Pennsylvania.

we hesitate to speculate on the nature of the stress systems during the cupping of non-directional metal.

In the last paragraph of his discussion, Dr. Wilson asks for a description of the textures found in copper, produced by different schedules, which eared in different ways. The texture of the strips about which Dr. Wilson inquired can be described as:

The strip rolled 25 per cent from completely cubically aligned copper and then annealed (eared at 45°) has a complex structure, which is described in reference 18.

The other strip, which eared at 45° to the rolling direction, has an unknown texture.

The strip annealed at 900°F. , rolled 16 band-S numbers, and annealed at 1200°F. , which eared at 0° and 90° to the rolling direction, had, according to Fig. 21b, 60 per cent cubic alignment.

Mr. Edmunds has shown a particular interest in the question of whether a second orientation is necessary to account for the minimum in the upper curve of Fig. 20. The slope sigma should be unity in the rolling direction if: (1) the metal is randomly oriented, (2) the metal is ideally cubically aligned, (3) the metal is nonideally cubically aligned but shows random scatter about the ideal orientation, or (4) is composed of various fractions of 1, 2 or 3. That this is true, is, as Mr. Edmunds pointed out, because fourfold symmetry exists about the rolling direction.

Anything that would destroy a fourfold symmetry around the rolling direction would cause sigma to deviate from unity (for tests taken in the rolling direction). Such factors would include: (1) mechanical fibering of certain types, (2) anisotropic grain shapes, (3) orientations not having a fourfold symmetry around the rolling direction.

This list includes only the most probable factors that might have entered into our work. We are quite certain that factor 1 can be neglected: great care was taken in preparing the samples, and no evidence of mechanical fibering appeared either in the micrographs, during shearing (blanking) or cupping, nor did examination of fractured tensile specimens reveal any fibering. The effect of factor 2 perhaps cannot be neglected. It is, however, the authors' opinion—opinion only—that the effect is a minor one. This leaves factor 3—orienta-

tions not having a fourfold symmetry around the rolling direction. Mr. Edmunds, in his second paragraph, has suggested—over and above the generalization of a texture having “twofold symmetry”—the presence of a $(001)[x\bar{y}0]$ (where $x \neq 1, 0, 1$ and $y \neq 1, 0, 1$) texture. Another texture was referred to by Mr. Howald in his reply: $(011)[2\bar{1}1]$. The choice between the two rests on rather meager data, as Mr. Howald has indicated, but appears to favor the latter.

We agree with Professor Norton on the importance of the stress system, and most eagerly would welcome any information he could obtain by means of X-rays. We would be glad to supply him with blanks or strip samples of 100 per cent cubically aligned material should he care to work on the problem.

We have already alluded, in our reply to Dr. Wilson's discussion, to work that we have undertaken on the stress state in the case of cupping “squared” blanks. Our method consists in: (1) an analysis of the strain rates developed during cupping and (2) the application of the St. Venant equations, by means of a graphical method recently developed²¹ to determine the stresses acting. The method is restricted to metals that obey or approximate St. Venant's equations; i.e., nondirectional metal. (We would imagine that any stress analysis by means of X-rays of metal other than nondirectional would be complicated because of the anisotropy of elastic constants, etc., etc.) It would be of interest to determine the stress systems involved in cupping by two such different methods.

Mr. Howald already has answered Dr. Brick's specific question. We should like to repeat, however, the remark made in the paper; i.e., the sigma values are predicated on a stress state of simple tension, which is completely different from that existing during cupping, and, secondly, the cupping operation sets up certain conditions of continuity and comparability of which no account is taken in a tensile test on the sigma values. Therefore we regard it as a fortuitous coincidence that maxima in the sigma curves are located in the same directions as are the ears of drawn cups in so many instances. We do, have however, experiments designed to deter-

²¹ Baldwin: This volume, p. 55.

mine the behavior of anisotropic metal under combined stresses and this information in conjunction with a knowledge of the stress system operating during cupping should give then a coherent explanation of the mechanisms involved.

By way of historical interest, we have found a description of anisotropic contraction in the cross section of a tensile specimen. In 1927, L. Weiss³² reports, "... a rolling experiment was undertaken in which an aluminum strip 19.5-mm. gauge was cold-rolled to 9.93 mm. ... From this strip a test cylinder was machined so that in compression faces coincided with the rolled surfaces. ... An unusual phenomenon was observed, which should be mentioned. The sample of hard-rolled aluminum became completely oval (on compression) as shown in Fig. 23. To determine how the axes of the ellipse lay with respect to the rolling direction, a new sample was prepared in which the rolling direction was indicated by a scratched line on the compression face. The result is shown in Fig. 23. At this time, I should like to recall a tensile specimen which I prepared a number of years ago; it was machined out of a 30-mm. thick

aluminum strip. Even though this specimen was annealed before testing, the cross section of the fracture deformed to an oval as shown in Fig. 23."

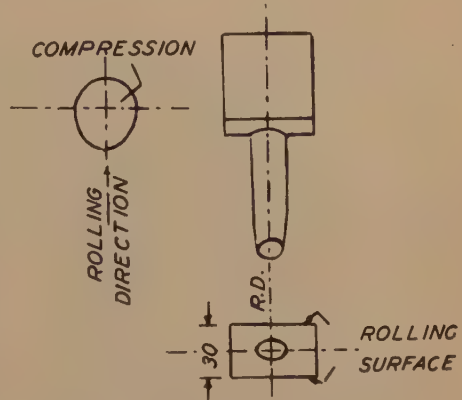


FIG. 23.—SKETCH FROM WEISS' PAPER.³²

From a study of the sketch given in Fig. 23, it would appear that the slope sigma for Weiss' tensile specimen (taken at zero degrees to the rolling direction) was less than unity. Weiss did not, however, investigate the properties of the same strip when tested at other angles to the rolling direction.

³² Weiss: *Ztsch. Metallkunde* (1927) 19, 61.

Diffusion of the Stable Isotopes of Nickel in Copper

BY WILLIAM A. JOHNSON,* JUNIOR MEMBER A.I.M.E.

(Chicago Meeting, February, 1946)

THE mathematical analysis of diffusion curves in solid metals is carried out ordinarily by analogy with the flow of heat in a continuous medium and no account is taken of the fact that the materials involved are composed of discrete particles that move discrete distances at irregular intervals. It is possible to treat the problem on the basis of simple assumed atomic mechanisms, in which case, because of the small scale of the elementary process compared to the gross effects observed experimentally, the two procedures lead to the same expression for the variation of concentration with distance. Thus, for engineering purposes, the usual methods are quite satisfactory. If, on the other hand, our purpose is to go beyond the mere collection of data, however desirable this may be, it is necessary to recognize and understand the factors that are of fundamental importance.

One factor that has not hitherto been considered when dealing with solid metals is the difference in atomic weights of the isotopes of a single metal. While all the atoms of a given element are alike chemically, their weights may vary by a small but significant amount, and atoms of different weights may have different diffusion rates. With gases this variation in isotopic weight produces a change in the rate of diffusion by a factor inversely proportional to the square root of mass.

While, except for the lightest gases, this is not a large effect, it is, for example, sufficient to permit a considerable concentration of one isotope at the expense of others. If metals exhibit a similar phenomenon, some modification of the analysis of the diffusion process will be required, since the different isotopes of a given metal will have different probabilities of moving and the heat-flow analogy will contain a fundamental error. This situation cannot be rectified by using a diffusion coefficient based on the average probability of moving, and it can be shown that even when the diffusion coefficient is independent of composition, the diffusion curve will not agree with the simple theory except in the rare cases where only one isotope exists; e.g., gold. If, however, the mass effect in the solid state were no larger than in the gaseous, the errors arising therefrom in the analysis of ordinary diffusion curves would be quite negligible. Nevertheless, our desire to obtain all possible information concerning the details of the diffusion process, and the possibility of diffusion in the solid state as a means for separating isotopes are cogent reasons for undertaking an experimental study to determine whether isotopes of different masses diffuse at different rates.

EXPERIMENTAL PROCEDURE

If isotopes of different masses diffuse at different rates, the ratio of the concentration of one relative to another will vary with the distance from the diffusion inter-

Manuscript received at the office of the Institute Dec. 14, 1945. Issued as T.P. 2007 in METALS TECHNOLOGY, June 1946.

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face and measurement of this ratio will determine the magnitude of the effect. Although a change in ratio might be detected, by very precise chemical analysis,

be analyzed is admitted by a capillary leak, and the electron beam ionizes some of the molecules of the gas sample. A difference in potential draws the ions

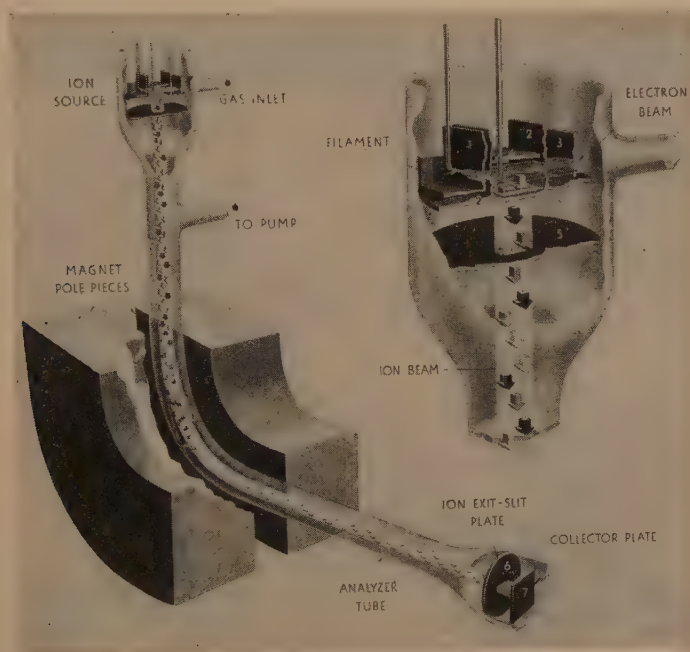


FIG. 1.—PHANTOM VIEW OF MASS SPECTROMETER, ONE GENERAL AND THE OTHER A CLOSEUP OF THE IONIZING STRUCTURE.

as a change in atomic weight, much more satisfactory data are furnished by the mass spectrometer. This instrument, by measuring the relative abundance of each isotope with an accuracy better than one per cent, provides far greater sensitivity than any chemical method, and permits also the accurate determination of the change in each individual isotope and not merely the average effect over all isotopes.

A spectrometer designed primarily for the analysis of gases was available and the details of the diffusion experiment were determined to a large extent by the limitations of this instrument, which is shown schematically in Fig. 1. The operation of a mass spectrometer of this type is briefly as follows: The sample of gas to

through the first slit and accelerates them to the second slit, where they emerge as a beam. This ion beam travels straight down the tube until the magnetic field bends the ions into a circular path. By proper adjustment of the ion accelerating voltage and magnetic field, ions of a particular mass (i.e., mass divided by charge) follow the curve of the tube and emerge through the exit slit. Here the ions are caught by a Faraday cage and the current corresponding to this particular mass is measured. Since the current is proportional to the number of ions, the ratio of the currents for different masses is the ratio of the relative abundance of the different masses, and thus any change in the concentration of one relative to another is readily measured.

Metals are not very volatile at ordinary temperatures and the choice of the metal to be studied had to be made on the basis of the possibility of vaporizing it in sufficient quantity to permit analysis. Moreover, it would seem desirable that a metal of general familiarity be chosen. Of the various diffusion combinations considered, nickel-copper seemed most suitable, for diffusion in this system has been studied, the metals and their alloys are well known, and the volatile nickel carbonyl furnished a convenient means for introducing the metal vapor into the spectrometer. In the course of the experimental work, however, it was discovered that the choice was not an entirely satisfactory one, since nickel carbonyl decomposes readily under the low pressure employed and deposits nickel in the apparatus. For this reason the data are neither as accurate nor as voluminous as might have been obtained with another compound, although they indicate clearly that there is a small mass effect in diffusion in solid metals.

The diffusion specimen was prepared by electroplating a nickel layer 0.012 in. thick on an O.F.H.C. copper cylinder 0.950 in. in diameter by 3 in. long. To secure an adherent deposit, an electrolyte of nickel sulphate and nickel chloride was operated at 60°C. with a current density of about 30 ma. per sq. in. To prevent blistering, the plated specimen was heated slowly (50°C. per hour) and then diffused for 3.4 days at 1053°C. in "Ammogas." The specimen was mounted in a lathe on its original centers and 20 layers of from 0.0015 to 0.0020 in. thickness were machined off. The layers were analyzed for copper electrolytically and the residue of nickel sulphate was set aside for conversion to nickel carbonyl.

The preparation of nickel carbonyl, $\text{Ni}(\text{CO})_4$, was found to be much more difficult than had been anticipated on the basis of textbook accounts. The standard procedure is to pass pure carbon monoxide

at atmospheric pressure over finely divided nickel powder at 25° to 75°C., separating the gaseous carbonyl from the excess carbon monoxide by condensation in dry ice or liquid air. To secure a very large surface of nickel for reaction, it has been found best to start with nickel oxalate or formate and reduce this with hydrogen at the lowest practicable temperature—about 200°C. The yield under the optimum conditions that could be established was very small, perhaps 0.1 per cent of the nickel being converted to carbonyl per hour. Since initial samples of nickel as small as 50 mg. were to be used and samples of carbonyl containing 25 mg. of nickel were the smallest for which the mass spectrometer would provide satisfactory results, a rather different method of preparing carbonyl had to be employed.

According to Dr. Owen G. Bennett, the difficulty with the usual methods of reducing nickel oxide, oxalate or formate is their failure to produce a nickel powder with a sufficiently great specific surface and free from a very thin oxide layer. A much more suitable nickel powder can be obtained by evaporation of a nickel amalgam.¹ This is prepared by electrolyzing slightly acid nickel sulphate or chloride with a mercury cathode and an insoluble anode, the volume of mercury being chosen to yield an amalgam containing about 2 per cent nickel. The amalgam is washed and dried and immediately transferred to a glass vacuum apparatus, shown schematically in Fig. 2, in which the mercury is distilled off in vacuo at about 250°C. The residue is a spongy mass of very fine nickel powder that reacts quickly with carbon monoxide at about 50°C. Since the reaction is exothermic, no additional heat need be supplied when the nickel amounts to several hundred grams, but with only a gram or less, as in the present case, additional heat must be supplied.

¹ References are at the end of the paper.

Too high a temperature should be avoided, since the carbonyl decomposes to an appreciable extent as the temperature rises above 75°C .

number of the diffusion layers cut from the specimen and were kept in sealed-off glass tubes because of the volatile and poisonous nature of the compound.

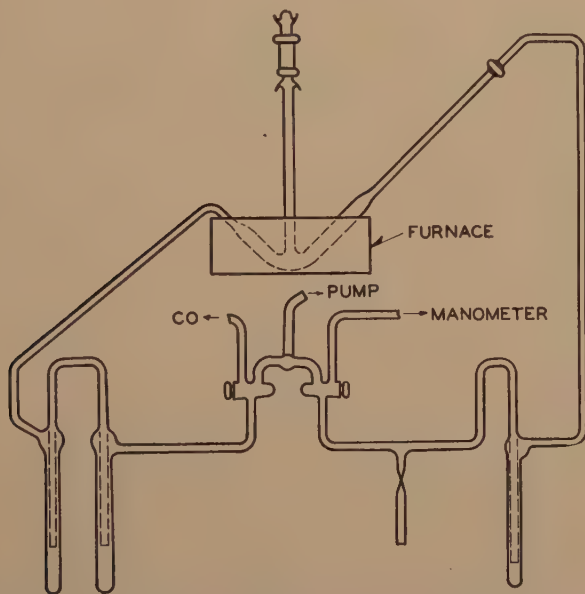


FIG. 2.—SCHEMATIC DIAGRAM OF GLASS APPARATUS FOR PRODUCTION OF NICKEL CARBONYL.

An essential factor in the success of the reaction is a supply of very pure carbon monoxide, the most harmful impurities being water, carbon dioxide, and sulphur. Commercial tank carbon monoxide was passed through Ascarite (CO_2 absorbent) and Anhydrone (H_2O absorbent), copper chips at 500°C ., Ascarite, Anhydrone, and finally a liquid-air trap; common sulphur-bearing gases would be largely absorbed by several of these reagents. Gas so purified did not form a harmful reaction layer on the nickel powder even after 24 hr. exposure. The process so carried out was entirely successful, some 50 per cent of the nickel being transformed to carbonyl in 5 hr., and 75 per cent in 10 hr. Amounts of nickel as small as 50 mg. were sufficient to prepare enough carbonyl for analysis in the spectrometer. Samples of carbonyl were prepared by this method from a

The mass spectrometer used was devised by Dr. J. A. Hipple² for gaseous specimens. Preliminary experiments indicated that difficulty would be experienced in securing large ion currents and consequently these were measured with a type-K potentiometer rather than with the automatic recorder. The original intention was to measure the relative abundance of all five nickel isotopes (Ni^{58} , Ni^{60} , Ni^{61} , Ni^{62} and Ni^{64} , of which the atomic weights are, respectively, 58, 60, 61, 62 and 64) on about 10 of the layers, but difficulties in the operation of the spectrometer with nickel carbonyl severely curtailed this program. Although at atmospheric pressure nickel carbonyl is stable at temperatures up to about 75°C ., at the pressures of a few millimeters of mercury used in the spectrometer it decomposes to an appreciable extent at room temperature.

As a deposit of metallic nickel built up on the glass parts of the apparatus, through spontaneous decomposition, the measured abundance of the heavier isotopes de-

ments of the abundance of Ni^{61} and Ni^{64} . Moreover, it appeared that Ni^{61} was not completely resolved from the much more abundant Ni^{60} , and that unknown impuri-

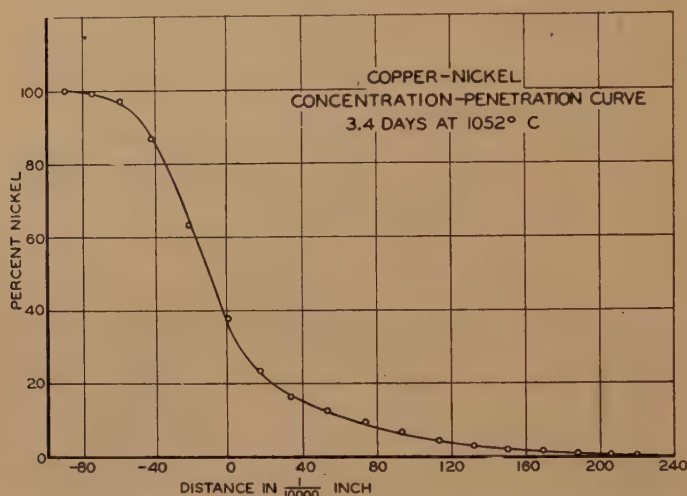


FIG. 3.—CONCENTRATION-PENETRATION CURVE FOR COPPER-NICKEL SPECIMEN AFTER 3.4 DAYS AT 1052°C.

creased relative to the lighter, but whether this was selective decomposition or an electrical effect caused by the presence of a conducting film was not discovered. Since this effect did not become serious until carbonyl had been in the apparatus for perhaps 10 hr., the difficulty was circumvented by periodically washing out the glassware with nitric acid. As a check on the proper functioning of the apparatus, a standard sample of ordinary nickel carbonyl was checked frequently. Unfortunately, a deposit of nickel finally built up in the spectrometer tube itself, shorting the insulation and ending the useful life of the tube. Although additional data would have been desirable, they would not justify the probable destruction of a new tube.

Because of the high molecular weight of nickel carbonyl, and its partial decomposition to carbon monoxide, difficulty was experienced in obtaining sufficiently large ion currents for accurate measure-

ties affected the apparent abundance of Ni^{64} . Thus, only the data for the three isotopes Ni^{58} , Ni^{60} , and Ni^{62} are regarded as reliable.

TABLE I.—*Chemical Analyses of Layers from Diffusion Specimen*

Layer No.	Average Radius, In.	Nickel, Per Cent
1	0.4849	99.90
2	0.4833	99.25
3	0.4818	97.15
4	0.4800	87.02
5	0.4780	63.54
6	0.4760	37.60
7	0.4743	23.05
8	0.4725	16.44
9	0.4705	12.62
10	0.4685	9.12
11	0.4665	6.88
12	0.4645	4.25
13	0.4626	2.97
14	0.4608	2.16
15	0.4589	1.52
16	0.4570	1.02
17	0.4553	0.68
18	0.4538	0.51

Certain corrections are necessary to obtain absolute values from the ion currents measured with the spectrometer.

Upon electron bombardment in the spectrometer, nickel carbonyl decomposes into a number of different ions, among which Ni^+ and $\text{Ni}(\text{CO})_2^{++}$ are particularly impor-

since only a change in ratio was to be detected, this correction, being nearly constant, could have been neglected. Because of the small amount of Ni^{64} in

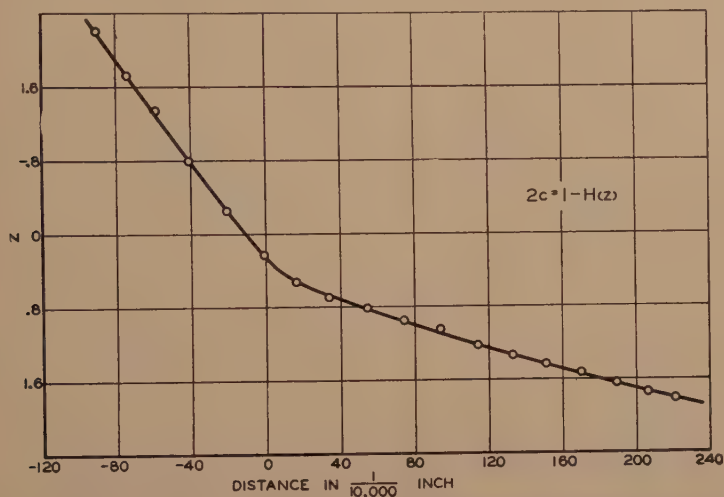


FIG. 4.—RELOT OF DATA IN FIGURE 3 USING PROBABILITY CONCENTRATION SCALE.

tant. The ion $\text{Ni}^{60}(\text{CO})_2^{++}$ being doubly charged, behaves like a particle of half its mass; i.e., one half of 116 or 58, and is collected as though it were Ni^{58+} . A similar situation exists for $\text{Ni}^{64}(\text{CO})_2^{++}$ which appears as Ni^{60+} , but no complications arise for Ni^{61} , Ni^{62} , or Ni^{64} . Even this error would not have to be taken into account in the present experiment if the isotopic ratios of the several samples remained constant, but since the data show a small change from sample to sample, a suitable correction was made. The amounts of masses 57 ($\text{Ni}^{58}(\text{CO})_2^{++}$), 114 ($\text{Ni}^{58}(\text{CO})_2^{+}$) and 116 ($\text{Ni}^{60}(\text{CO})_2^{+}$) were measured and the amount of mass 58 ($\text{Ni}^{60}(\text{CO})_2^{++}$) was found by simple proportion on the assumption that the ratio of $\text{Ni}(\text{CO})_2^{+}$ to $\text{Ni}(\text{CO})_2^{++}$ is independent of the mass of the nickel isotope. When this value was subtracted from the total observed mass 58, the balance was that due to Ni^{58} . The correction amounted to about 2 per cent and would be important if the absolute ratios of the isotopes were necessary;

the samples, the correction to Ni^{60} arising therefrom was negligible.

TABLE 2.—Coordinates of Smoothed Concentration-penetration Curve

Distance from Interface, 1/10,000 In.	Nickel, Per Cent	Distance from Interface, 1/10,000 In.	Nickel, Per Cent
220	0.503	50	13.04
210	0.620	40	15.16
200	0.768	30	17.60
190	0.948	20	20.97
180	1.170	10	26.18
170	1.439	0	35.02
160	1.767	-10	47.35
150	2.164	-20	61.41
140	2.64	-30	76.64
130	3.22	-40	85.30
120	3.90	-50	92.52
110	4.70	-60	96.69
100	5.65	-70	98.74
90	6.75	-80	99.59
80	8.03	-90	99.88
70	9.49	-100	99.97
60	11.16		

EXPERIMENTAL RESULTS

The chemical analyses and positions of the layers machined from the diffusion specimen are listed in Table 1 and are plotted

in Fig. 3. By making the substitution

$$2c = 1 - H(z)$$

where c is the concentration, and $H(z)$ is the probability integral, the data can be plotted (Fig. 4) in a manner more suitable for drawing the best smooth curve through the datum points. Values of z were read from this curve and adjusted slightly to cause successive differences to vary regularly; the corresponding concentrations are given in Table 2. The smoothed coordinates so obtained were used for calculating the diffusion coefficient, and the isotopic ratios to be expected for several assumed variations of diffusion coefficient with mass.

The unsymmetrical shape of the diffusion curve indicates that the diffusion coefficient is dependent on composition and must be evaluated by a special method, for example that given by Boltzmann³ and Matano.⁴ The diffusion equation is

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right)$$

where D is not a constant, but a function of c . It is convenient to seek a solution of this equation in which c is a function of

$$\lambda = \frac{x}{\sqrt{t}}$$

alone; that is,

$$c(x, t) = c \left(\frac{x}{\sqrt{t}} \right) = c(\lambda)$$

Trying this assumption in the diffusion equation, the following is obtained:

$$\frac{d}{d\lambda} \left(D \frac{dc}{d\lambda} \right) + \frac{1}{2} \lambda \frac{dc}{d\lambda} = 0 \quad [1]$$

The fact that the variables x and t have disappeared shows that the assumption that there is a solution of the diffusion equation of the form $c \left(\frac{x}{\sqrt{t}} \right) = c(\lambda)$ is correct.

If the equation is transformed so that λ is the dependent variable and c the inde-

pendent variable, there results

$$\frac{d}{dc} \left(D \frac{d\lambda}{dc} \right) + \frac{1}{2} \lambda = 0$$

which gives the equation

$$D = -\frac{1}{2} \frac{d\lambda}{dc} \int_{c_0}^c \lambda dc + A$$

in which A is a constant of integration.

Rewriting, with λ set equal to $\frac{x}{\sqrt{t}}$, the equation becomes

$$D = -\frac{1}{2t} \frac{dx}{dc} \int_{c_0}^c x dc \quad [2]$$

In this the constant A has been reduced to zero by choosing the point at which $x = 0$ such that

$$\int_{c_0}^{c_m} x dc = 0$$

where c_0 and c_m are, respectively, the minimum and maximum concentrations in the specimen.

When distance x is given in inches or centimeters, the concentration should be expressed as weight per unit volume; since the density of copper-nickel alloys changes very little with composition, it is satisfactory to express concentration as fraction by weight. Using Eq. 2, the diffusion coefficient was calculated from the data in Table 2, with results shown in Fig. 5. The only other determination for copper-nickel alloys, that of Grube and Jede as recalculated by Matano, is also shown; the writer corrected this from 1025°C. to 1052°C. using the activation energy of 29,800 cal. While the agreement between the two curves may seem poor, the great sensitivity of the calculated diffusion coefficient to slight variations in the diffusion curve makes the differences not unreasonable. It is believed that the irregularity in the neighborhood of 85 per cent copper is not of significance; a suitable change in two of the points on the diffusion curve by an amount not exceeding the

experimental error would remove this irregularity.

The isotopic ratios of four of the layers and of a standard sample of ordinary nickel, as determined with the mass spectrometer, are given in Table 3, with an estimate of the probable error based on the internal consistency of about eight measurements of each ratio. This estimate of error is lower than the total error, since it includes only the random errors occurring during a set of measurements and omits any systematic errors; in view of the difficulties in the operation of the spectrometer arising from the decomposition of the carbonyl, probable errors perhaps twice as large as those given might be more reasonable. The data indicate that the isotopic ratios were measured with an accuracy somewhat better than one per cent, but since the changes in ratio from specimen to specimen are small, the accuracy in terms of this change is not good. Nevertheless, the data show conclusively that a change in isotopic ratio was produced by diffusion, and, since there is an enrichment of the lighter isotopes of nickel on the copper side of the interface and an impoverishment on the nickel side, that the lighter isotopes diffuse more rapidly than the heavier.

TABLE 3.—*Isotopic Ratios of Layers from Diffusion Specimen*

Layer No.	Nickel, Per Cent	Ni ⁵⁸ /Ni ⁶⁰	Ni ⁵⁸ /Ni ⁶²
5	63.54	2.556 (1 ± 0.0008)	18.49 (1 ± 0.0022)
9	12.62	2.578 (1 ± 0.0012)	18.73 (1 ± 0.0120)
12	4.25	2.603 (1 ± 0.0020)	19.02 (1 ± 0.0022)
14 + 15	1.80	2.650 (1 ± 0.0012)	19.77 (1 ± 0.0011)
Standard	100	2.557 (1 ± 0.0020)	18.55 (1 ± 0.0032)

The most satisfactory means for discovering the law expressing the effect of mass on the diffusion coefficient would be a set of curves showing the variation of diffusion coefficient with composition for each of the five isotopes. Study of these

curves would permit the derivation of the empirical relation between diffusion coefficient, mass and composition; it would be possible to discover, for example, if the

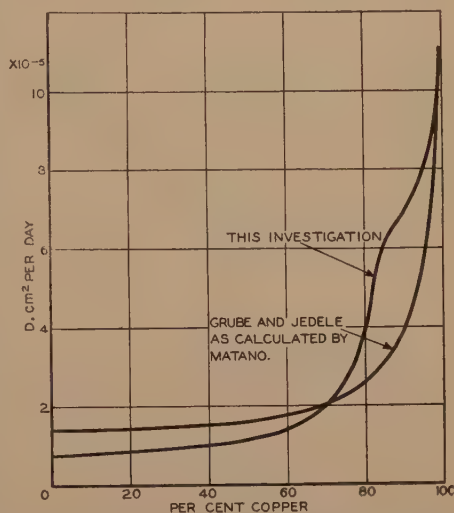


FIG. 5.—*Variation of Diffusion Coefficient with Composition at 1052°C., Copper-Nickel System.*

TABLE 4.—*Change in Isotopic Ratio Produced by Diffusion*

Layer No.	Nickel, Per Cent	$\left(\frac{\text{Ni}^{58}}{\text{Ni}^{60}}\right)_{\text{Std.}} \times \left(\frac{\text{Ni}^{60}}{\text{Ni}^{58}}\right)_{\text{Spec.}}$	$\left(\frac{\text{Ni}^{58}}{\text{Ni}^{62}}\right)_{\text{Std.}} \times \left(\frac{\text{Ni}^{62}}{\text{Ni}^{58}}\right)_{\text{Spec.}}$
5	63.54	1.0004 ± 0.0022	1.0032 ± 0.0039
9	12.62	0.9919 ± 0.0023	0.9904 ± 0.0124
12	4.25	0.9823 ± 0.0028	0.9753 ± 0.0039
14 + 15	1.80	0.9649 ± 0.0023	0.9383 ± 0.0034
5	63.54	-0.0004 ± 0.0022	-0.0032 ± 0.0039
9	12.62	+0.0081 ± 0.0023	+0.0096 ± 0.0124
12	4.25	+0.0177 ± 0.0028	+0.0247 ± 0.0039
14 + 15	1.80	+0.0351 ± 0.0023	+0.0617 ± 0.0034

effects of mass and composition are so related that the diffusion coefficient can be written as the product of two factors, one expressing only the effect of mass, the other expressing only the effect of composition. If the chemical analysis and complete isotopic constitution of each layer were known, concentration-penetration curves for each isotope could be

constructed and the individual diffusion coefficients calculated therefrom as shown above. Since, because of difficulties with the spectrometer, it was not possible to obtain

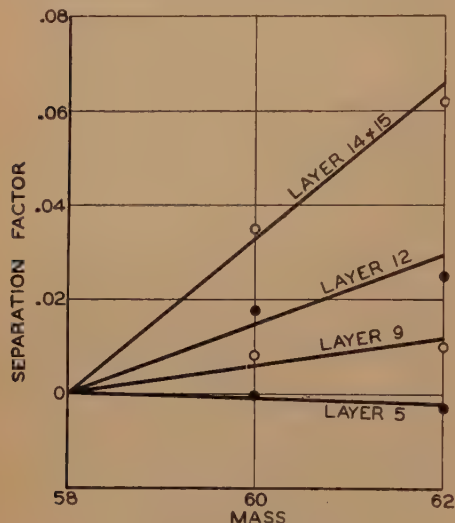


FIG. 6.—VARIATION OF SEPARATION FACTOR WITH MASS AT SEVERAL DISTANCES FROM DIFFUSION INTERFACE.

Concentration of the isotope of mass 58 is taken as the reference standard.

all the data required, this general method of attack had to be abandoned, and the data were merely examined to determine whether they were in agreement with predictions made on the basis of certain reasonable assumptions concerning the effect of mass. While this procedure cannot be justified as proving the validity of an assumed law that yields correct predictions—since the same special predictions might be obtained from a different law—it does provide almost the only means for interpreting the available data.

The dependence of the diffusion coefficient on mass and composition was assumed to be of the form

$$D_M = M^{-n}D(c)$$

where D_M is the diffusion coefficient of an isotope of mass M , n is an index to be determined experimentally and $D(c)$ is the concentration dependence. Two choices

are available regarding the form of $D(c)$. It may be assumed that the rate of diffusion of a given isotope depends on the concentration of only isotopes of identical mass, or it may depend on the concentration of all chemically similar isotopes. The latter seems the more reasonable assumption and the detailed calculations below are based on it; certain consequences of the former assumption are mentioned, although the relatively easy calculations on which they are based are omitted. According to the assumed law, the absolute values of the diffusion coefficients will vary from place to place as the composition changes, but their ratios will be constant.

On the basis of the assumed dependence of D_M on mass and composition, certain predictions can be made concerning the variations in isotopic ratios in the several layers. Two of these may be tested with the data. The effect of mass on the isotopic ratios within a single layer, and the effect of composition (or distance from the interface) on the relative abundance of a single isotope. In order to make these predictions quantitative, it is convenient to have an expression for the variation of concentration with distance as a function of the diffusion coefficient. It may be verified directly, by substitution, that the following equation,⁵

$$c = A \int_0^\lambda \frac{d\lambda}{D} \exp. \left[- \int_0^\lambda \frac{\lambda d\lambda}{2D} \right] + B \quad [3]$$

in which A and B are constants of integration, is a solution of Eq. 2, and is, consequently, the expression sought. In this equation, D is to be considered a function of

$\lambda = \frac{x}{\sqrt{t}}$, and may be so expressed by using

the curves in Figs. 3 and 5. However, in order to determine the concentration penetration of a single isotope from this equation, it is necessary first to have the diffusion coefficient for a single isotope. Examination of the data shows that the diffusion coefficient for Ni^{58} , the most abundant

isotope, is indistinguishable experimentally from that for nickel, and the various curves shown may be taken equally well for Ni^{58} or for nickel. Then, for a particular isotope,

$$c_K = A_K \int_0^\lambda \frac{d\lambda}{KD} \exp. \left[- \int_0^\lambda \frac{\lambda d\lambda}{2KD} \right] + B_K \quad [4]$$

where c_K is the concentration of an isotope of mass M_K , which has a diffusion coefficient of KD where

$$K = \left(\frac{M}{58} \right)$$

and the constants A_K and B_K are determined by the boundary conditions.

Since K can be evaluated for any assumed value of n and D is known as a function of λ , it is possible to calculate the diffusion curve for each isotope. However, in view of the small variation in isotopic ratios found experimentally, the curves for the different isotopes would be nearly identical, and the proposed numerical calculation very difficult to perform with sufficient accuracy. Since what is really wanted is the change in diffusion curve with change in mass, it is more satisfactory to expand the expression for concentration in terms of the parameter K . The integrand may be expanded conveniently by the following method:

$$\text{Let} \quad \int_0^\lambda \frac{\lambda d\lambda}{2D} = G(\lambda)$$

and

$$\exp. \left[- \frac{G(\lambda)}{K} \right] = R(\lambda, K)$$

Then

$$R(\lambda, K) = R(\lambda, 1) + (K-1) \frac{\partial R}{\partial K} \Big|_1 + \frac{(K-1)^2}{2} \frac{\partial^2 R}{\partial K^2} \Big|_1 + \dots$$

And

$$c_K = \frac{A_K}{K} \int_0^\lambda \frac{R(\lambda, 1)}{D} d\lambda + \frac{A_K}{K} (K-1) \int_0^\lambda \frac{R(\lambda, 1)}{D} G(\lambda) d\lambda + \frac{A_K}{2K} (K-1)^2 \int_0^\lambda \frac{R(\lambda, 1)}{D} G(\lambda) [G(\lambda) - 2] d\lambda + \dots + B_K \quad [5]$$

For convenience put

$$\int_0^\lambda \frac{AR(\lambda, 1) G(\lambda)}{D} d\lambda = I_1(\lambda)$$

$$\int_0^\lambda \frac{AR(\lambda, 1) G(\lambda)}{D} [G(\lambda) - 2] d\lambda = I_2(\lambda)$$

These integrals can be evaluated numerically by using values from the diffusion curve. The following relations are convenient for this calculation:

$$\frac{AR(\lambda, 1)}{D} = \frac{dc}{d\lambda}$$

$$G(\lambda) = \ln A - \ln \left(D \frac{dc}{d\lambda} \right)$$

$$G(0) = 0$$

With the aid of the numerical values and

$$I_1(-\infty) = 0.3572 \quad I_2(-\infty) = -0.1393$$

$$I_1(+\infty) = -0.1307 \quad I_2(+\infty) = 0.0822$$

the boundary conditions Eq. 5 can be put

$$c_K = 1 \text{ at } \lambda = -\infty$$

$$c_K = 0 \text{ at } \lambda = +\infty$$

in a form suitable for calculating the diffusion curve if terms higher than the second order be neglected. To determine whether this could be done without serious error, the values obtained with and without the second-order term were compared. This is done most conveniently by calculating the separation factor as a function of distance, where the separation factor S is defined as

$$S_M = 1 - \left(\frac{\text{conc. Ni}^M}{\text{conc. Ni}^{58}} \right)_{\text{final}} \times \left(\frac{\text{conc. Ni}^{58}}{\text{conc. Ni}^M} \right)_{\text{initial}}$$

The first-order approximation is

$$S_M = - \frac{(K-1)}{1 + 0.4879(K-1)} \left[\frac{0.1307 + I_1(\lambda)}{C} - 0.4879 \right] \quad [6]$$

and the second-order approximation is

$$S_M = - \frac{(K-1)}{1 + 0.4879(K-1) - 0.1108(K-1)^2} \left[\frac{0.1307 + I_1(\lambda)}{C} - 0.4879 + (K-1) \left\{ \frac{K_2(\lambda) - 0.0822}{I_2(\lambda)2C} + 0.1108 \right\} \right] \quad [7]$$

A preliminary examination of the data indicated that K should have a value of nearly $\left(\frac{58}{M}\right)^{0.5}$ and a comparison of the values of S_M given by the two expressions for $K = \left(\frac{58}{62}\right)^{0.5}$ is shown in Table 5. The

showing that at a given distance from the interface, or at a given concentration, the separation factor depends only on the mass. Since

$$f(K) = \frac{K-1}{1 + 0.4879(K-1) - 0.1108(K-1)^2}$$

and K differs from unity by only a few per cent, $f(K)$ is nearly linear in K . Moreover, K is given approximately by

$$K = 1 + n \left(\frac{M-58}{58} \right)$$

and the separation factor is thus nearly linear in mass. Accurate calculations show that the separation factor for mass 60 is 50.8 per cent of the value for mass 62, as compared with the approximate value of 50.0 per cent obtained from the above equation. The agreement of the data with this relationship is tested in Fig. 6, and it is seen that for any composition, the variation of separation factor with mass is in good agreement with the assumed mass effect in diffusion.

Several methods are available for determining the best value of the index n . It was assumed that the best value of n is the one that minimizes the sum of the squares of the differences between the observed values of the separation factor and those calculated from Eq. 7. This criterion leads to a value of 0.48, which may be rounded off to 0.5. Thus the diffusion coefficient varies inversely with the square root of mass, as with gases. A

TABLE 5.—Comparison of Separation Factors Calculated from Several Equations
Mass 62, $n = 0.50$

x	Equation 6	Equation 7	Equation 8
-80	-0.0006	-0.0006	-0.0006
-60	-0.0027	-0.0027	-0.0028
-40	-0.0065	-0.0065	-0.0067
-20	-0.0083	-0.0083	-0.0075
0	-0.0039	-0.0039	0.0000
20	0.0040	0.0041	0.0062
40	0.0103	0.0104	0.0122
60	0.0169	0.0170	0.0175
80	0.0247	0.0248	0.0227
100	0.0334	0.0334	0.0307
120	0.0435	0.0431	0.0374
140	0.0529	0.0522	0.0451
160	0.0639	0.0629	0.0534
180	0.0752	0.0737	0.0615
200	0.0871	0.0848	0.0700

excellent agreement between the two approximations indicates that terms higher than the second may be safely neglected, and that even the second-order term is quite small.

An alternative procedure would be to expand the expression for concentration directly in terms of the mass, but the series so obtained is more cumbersome and converges less rapidly.

The equation for the separation factor may be written as

$$S_M = f(K)F(\lambda)$$

comparison of the experimentally observed values of the separation factor with those calculated on the basis of the inverse square root of mass law is given in Fig. 7.

The theoretical curve of separation factor versus distance calculated from this equation is listed in Table 5. It has a value of unity at 35 per cent nickel for all isotopes,

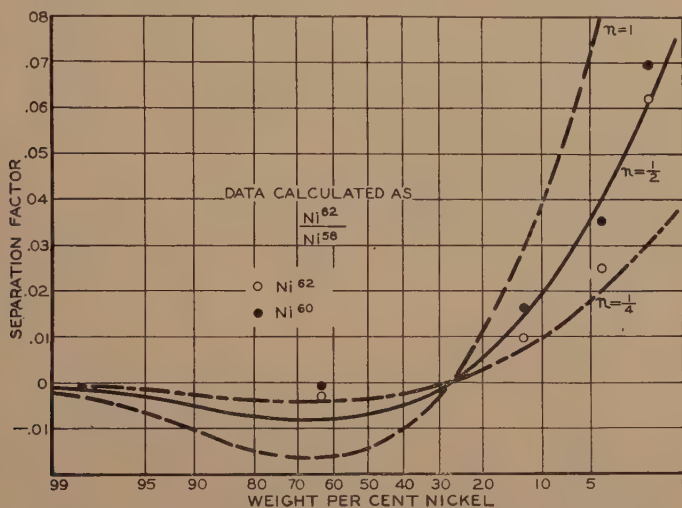


FIG. 7.—COMPARISON OF OBSERVED VALUES OF SEPARATION FACTOR WITH THOSE CALCULATED ON ASSUMPTION THAT DIFFUSION RATE VARIES INVERSELY WITH SQUARE ROOT OF MASS.

While the differences between the observed values and the calculated curve for $n = 0.50$ may appear large, the average deviation of all measurements is only 0.45 per cent, an excellent figure for this type of work with the mass spectrometer. The data are definitely in better accord with the curve for $n = \frac{1}{2}$ than for $n = \frac{1}{4}$ or 1, but it is clear that any value of n between 0.4 and 0.6 would fit the data about as well as 0.5.

If it is assumed that the composition effect depends only on the concentration of like isotopes, the calculations are very simple and lead qualitatively to the same results. If the concentration of an isotope is denoted by C_M , the separation factor is

$$S_M = 1 - \frac{C_M}{C_{58}} = 1 - \frac{C_{58} \left(\sqrt{\frac{M}{58}} \lambda \right)}{C_{58}(\lambda)}$$

where the diffusion curve for Ni^{58} is given by

$$c = C_{58}(\lambda)$$

while the curve in Fig. 7 has a value of unity at approximately 27 per cent nickel, this figure varying slightly with the mass of the isotope.

DISCUSSION OF RESULTS

It has been found experimentally that the relative abundance of the several isotopes of nickel is altered by diffusion into copper, and that the observed changes in isotopic constitution are best explained by assuming that the isotopes diffuse at rates inversely proportional to the square roots of their masses. This finding is not unexpected, for it is in agreement with the following generally accepted qualitative description of the diffusion process in solid metals. The diffusion coefficient may be considered to be the product of two factors, one representing the vibrational frequency ν of the atom—i.e., the frequency with which it approaches the energy barriers that interfere with its movement

to an adjacent lattice position—and the other a probability of its having sufficient energy to pass over this barrier. Thus

$$D = A v e^{-\frac{Q}{RT}}$$

The activation energy Q may be regarded as being principally a function of the valence electrons and is the same for all isotopes of a single element. The frequency term, however, may be regarded as proportional to the thermal frequency. If it is assumed that all atoms have the same energy content, the product of frequency squared and mass is constant and

$$\nu \sim \frac{1}{\sqrt{M}}$$

and hence

$$D = \frac{B}{\sqrt{M}} e^{-\frac{Q}{RT}}$$

ACKNOWLEDGMENT

It is a pleasure to thank Dr. L. W. Chubb for his interest in this work, Dr. Owen G. Bennett for his aid in devising a method for the production of nickel carbonyl, and Mr. A. G. Sharkey for making the mass spectrometer measurements.

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DISCUSSION

(Gerald Edmunds presiding)

J. CHIPMAN.*—This is a very interesting piece of work and it is going to assume more significance as radioactive isotopes become available for metallurgical studies. The time is surely approaching when such isotopes will play a prominent part in metallurgical research; and now it is clear just how the results

obtained with an isotope of a given mass can be interpreted in terms of an ordinary metal of mixed masses. It might be well to point out too that these observations are obtained on a substitutional solid solution. It would be a matter of very great interest to determine whether or not the same relationships will hold where the solute atom occupies an interstitial position. It is to be hoped that at some future time carbon 14 may be available for such studies.

G. EDMUNDS.*—I wonder if by this method we don't actually separate the isotopes. Perhaps we get the separation by this means so that we do not need to have the separate isotopes to begin with. Is that true?

W. A. JOHNSON (author's reply).—It is true that in many cases no separate isotope is required, since any difference in diffusion rate of the several isotopes can be evaluated from measurements on changes in isotopic ratios. This method would fail, however, when only one isotope exists naturally or where a single isotope greatly predominates. Even though ordinary carbon falls into the latter classification, containing about 99 per cent carbon 12 and 1 per cent carbon 13, the ease with which it can be analyzed in the mass spectrometer suggests that the use of a separate isotope, as proposed by Dr. Chipman, would not be necessary.

C. ZENER.†—I should like to ask a point of mathematics. Theoretically, how large a separation factor can you get as you go further out? Does it become greater?

W. A. JOHNSON.—On the copper side of the interface the separation factor for nickel will increase continuously from zero, approaching infinity as the concentration approaches zero. On the nickel side, the separation factor for nickel becomes negative and then increases, approaching zero as the concentration approaches pure nickel. Diffusion in the solid state thus offers the possibility of subdividing the diffused material into fractions of

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different isotopic ratios. Diffusion in the gas or liquid state is usually attended by agitation, which homogenizes the diffused material.

J. CHIPMAN.—I would like to ask Dr. Johnson whether he has ever given thought to the separation of isotopes in a solid metal by thermal diffusion—whether or not, say, a metal of mixed isotopic composition might be

partially separated by holding in a temperature gradient.

W. A. JOHNSON.—My knowledge of thermal diffusion in gases is too slight for me to do more than guess that the absence of strong convection currents in the solid state would seriously interfere with thermal diffusion as a separation method.

Solubility of Carbon in Molten Copper

BY MICHAEL B. BEVER,* JUNIOR MEMBER, AND CARL F. FLOE† MEMBER A.I.M.E.

(New York Meeting, October 1945)

THE possibility that carbon may be soluble in copper to a limited extent has been recognized for over a century. The quantitative investigation of this problem, however, requires more sensitive techniques than have formerly been available. Three recent developments have made possible more accurate determinations: the vacuum-fusion method of analysis, the production of copper of high purity and the availability of high-purity refractories, particularly graphite.

In addition to its obvious theoretical interest, the problem of carbon solubility in copper is of practical importance. In the production of copper and of high-copper alloys, carbonaceous covers are frequently used. If even minute amounts of carbon are dissolved, insoluble carbon oxide gases will be formed when such metals are poured under oxidizing conditions. A mechanism of this kind could well be one of the principal causes of gas porosity in casting copper-base products.

REVIEW OF LITERATURE

In 1823 Vivian¹ raised the question as to whether copper by overpoling becomes

This work represents a portion of a thesis submitted by M. B. Bever in partial fulfillment of the requirements for the degree of Doctor of Science from the Massachusetts Institute of Technology. Manuscript received at the office of the Institute Nov. 22, 1944. Listed for New York Meeting, February 1945, which was cancelled. Issued as T.P. 1802 in METALS TECHNOLOGY, September 1945.

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¹ References are at the end of the paper.

“combined with a minute portion of carbon.” Karsten² asserted, in 1832, that carbon reduces the high-temperature strength of pure copper, so that when the carbon content has reached 0.2 per cent the metal will be brittle at a dark red heat. According to Karsten, carbon contents of 0.05 per cent make it difficult to hot-work copper. He also reported that the specific gravity of copper is 8.8969 and that it increases to 8.9258 if the copper is cemented with carbon and then melted. He emphasized the difficulty of determining analytically the small amounts of carbon present in copper. The metal was removed by wet methods and the residue considered as carbon.

At Percy's request, Dick,³ in 1856, carried out various working tests on copper that had been in prolonged contact with carbon, and found that the working properties of the metal had not been affected. He also attempted to determine the presence of carbon analytically. In one experiment the copper was dissolved and the residue was fused with litharge, and in another essentially a combustion analysis was made on a copper sample. In a final experiment, a sample was dissolved and the residue subsequently subjected to a combustion analysis. Indications of as much as 0.005 per cent carbon were found, but Dick considered his work inconclusive largely because of the possible interference of sulphur.

Percy⁴ concluded, from Dick's experiments and from some experimental work of his own, that the solubility of carbon in copper had not been established with

certainty but that a minute quantity probably is soluble.

In 1873 Hampe⁵ reported analyses of copper that in the molten state had been held in contact with carbon for long periods. His conclusion was that copper does not dissolve a trace of carbon.

In 1904 Hempel⁶ reported that copper that had been in contact with carbon "at a white heat" for one hour retained 0.02 to 0.03 per cent carbon. His method of analysis consisted of dissolving the sample with aqua regia in a sealed tube and analyzing both the gases and the undissolved residue.

In 1905 Moissan⁷ found carbon on the surface of copper that had been superheated in contact with carbon. He reported a solubility of 1.60 per cent at the boiling point of copper. Work by Briner and Senglet⁸ on a metallographic determination of copper carbide is inconclusive.

Ruff and Bergdahl⁹ distilled copper in a small graphite crucible at various reduced pressures. They found a residue of "more or less macrocrystalline graphite" and considered this to be the carbon that had been in solution in the copper at the temperature of distillation. Results for three temperatures in the range of 2215° to 2300°C. were between 0.024 and 0.033 per cent.

In the discussion of a paper by Ellis¹⁰ on gases in copper, Ziegler stated that a "copper-carbon constitutional diagram must exist although the amounts of carbon may be expressed perhaps in ten-thousandths of a per cent."

In a paper on the determination of oxygen in copper by the vacuum-fusion method, Musatti and Ziliani¹¹ concluded from the literature that carbon is soluble in liquid copper. They implied that this was substantiated by the fact that they were able in a few minutes to eliminate oxygen quantitatively from a copper sample melted in a graphite crucible. This, however, cannot be considered

conclusive since the elimination of oxygen as carbon monoxide or dioxide could occur along the crucible walls by outward diffusion of the oxygen aided by convection currents in the metal.

In an unpublished thesis, Leonard¹² reported solubility values obtained by analyzing water-quenched samples of copper by the combustion method. His results indicated solubility of 0.003 to 0.004 per cent throughout the range of 1127° to 1650° C. without any marked effect of temperature.

Smart, Smith and Phillips¹³ found that the physical properties of high-purity copper were not affected by contact of the molten metal with carbon. As Chipman pointed out in the discussion, this indicates that the solubility of carbon in solid copper probably is exceedingly small. He referred to Leonard's positive results for liquid copper, which Hayward suggested may have been due to mechanically suspended graphite. Smart stated that mechanical inclusion would explain the failure of Leonard's results to vary with temperature.

In an investigation of the solubility of sulphur dioxide in molten copper, Floe and Chipman¹⁴ found indications that the OFHC copper used contained about 0.0004 per cent carbon. They reported difficulties in removing the last traces of carbon by oxidation. In the discussion of this paper, Skowronski pointed to the evidence that had been gradually accumulating in various laboratories to the effect that under certain conditions carbon may exist in copper. A. J. Phillips concurred with this and stated that "there is no question whatever that a small amount of carbon is soluble, at least in liquid copper." He felt that 0.003 per cent was too high, but that 0.0004 per cent was not surprising. He also mentioned that there is some evidence to prove that the smallest trace of oxygen will react with carbon in copper, thus removing it.

Murray and Ashley¹⁵ included a few analyses of carbon in copper in a paper dealing mainly with the determination of carbon in ferrous materials by the low-pressure combustion method. The copper samples were prepared by melting in graphite under nitrogen, but no information on temperatures or the method of quenching was given. Their results were 0.0017 and 0.0020 per cent.

Table 1 summarizes chronologically the published data on the solubility of carbon in copper.

TABLE 1.—*Chronological Summary of Data on the Solubility of Carbon in Copper*

Date	Author	Solubility of Carbon in Copper	
		Temperature	Per Cent
1832	Karsten		0.05-0.2
1856	Dick		0.005 ±
1861	Percy		"Minute proportion"
1873	Hampe		Nil
1904	Hempel	"White heat"	0.02-0.03
1905	Moissan	Boiling pt. of Cu	1.60
1919	Ruff and Bergdahl	2215°C.	0.024
		2245°C.	0.025
		2300°C.	0.033
1933	Ziegler ^a		0.0005 ± 0.0004
1939	Leonard		0.003
1942	Floe and Chipman ^b	1127°-1650°C.	0.0004
1944	Murray and Ashley		0.0017-0.0020

^a Estimate not based on experimental work.

^b OFHC copper.

EXPERIMENTAL METHODS

The investigation reported here was carried out by preparing copper samples saturated with carbon at various temperatures. These samples were then analyzed by a modified vacuum fusion method.

Preparation of Samples

As the solubility of carbon in liquid copper is small and decreases on cooling and solidification, the samples had to be prepared by rapid quenching from the saturation temperatures. Direct contact of the melt with air, water, steam and the oxides of carbon was undesirable. In

order to lessen the danger of mechanical inclusion of graphite, it was advisable not to pour the melt over graphite. Finally, a compact rod of about $\frac{3}{8}$ -in. diameter was desirable, since such a shape could be used in the analytical procedure without extensive mechanical preparation. For these reasons, casting the metal into a chilled mold, quenching crucible and metal under water, or pouring the metal into water were not tried. The methods that were employed were (1) gas quenching, (2) a modified water quench in which the metal remained under a protective atmosphere, and (3) continuous bottom casting.

Preparation by Gas Quenching.—The furnace used in making gas-quenched samples (Fig. 1) consisted of a vertical refractory tube. The crucible rested in the lower part of this tube and was heated by induction in an atmosphere of nitrogen. For quenching, the crucible was quickly raised into the upper, cool part of the tube and at the same time a large stream of nitrogen was flushed through the furnace.

There was some doubt as to whether or not several of the early samples had been oxidized slightly by the oxygen present as an impurity in the tank nitrogen. Therefore, starting with sample No. 7, it was decided to purify the nitrogen by passing it over copper gauze at 500° to 550°C. This purification process limited the flow of gas and raised its temperature, thus reducing the quenching rate. The crucibles and copper used and the method of temperature measurement are described under preparation of samples by water quenching.

Preparation by Water Quenching.—Samples Nos. 13 to 30 were prepared by water quenching. The method used combined the fast quenching action of water and the protection of an inert atmosphere. A crucible (8 in. long and $\frac{3}{4}$ in. in outside diameter) was suspended in a vertical

tube furnace through which a slow stream of nitrogen was passed. The crucible could be released so as to fall freely into a receptacle placed directly under the

the sample, and thus tended to retain quantitatively any dissolved carbon.

The details of the furnace are shown in Fig. 2. It consisted of an Alfrax tube *D*

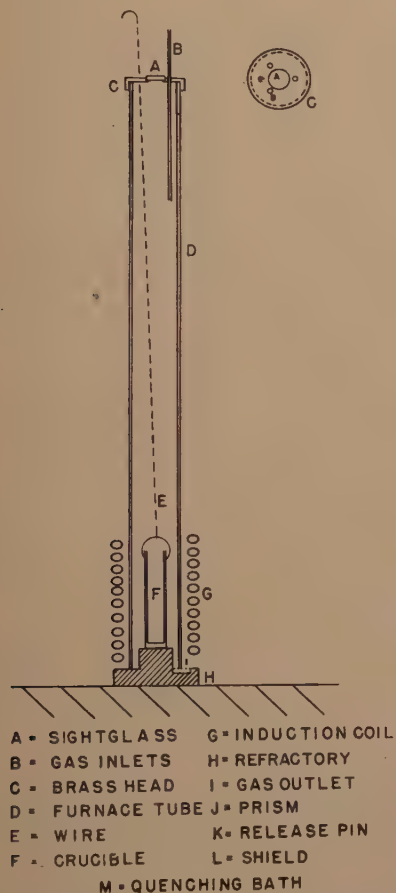


FIG. 1.—SCHEMATIC VIEW OF FURNACE FOR PREPARATION OF SAMPLES BY GAS QUENCHING.

furnace tube, containing cold water to a depth of about $5\frac{1}{2}$ in. In quenching, the crucible came to rest while its top still projected inside the furnace and the metal was thus protected by the inert atmosphere.

The quenching action seemed to be effective and the metal solidified in a few seconds. Moreover, the freezing process had the desirable characteristic of starting simultaneously along the entire surface of

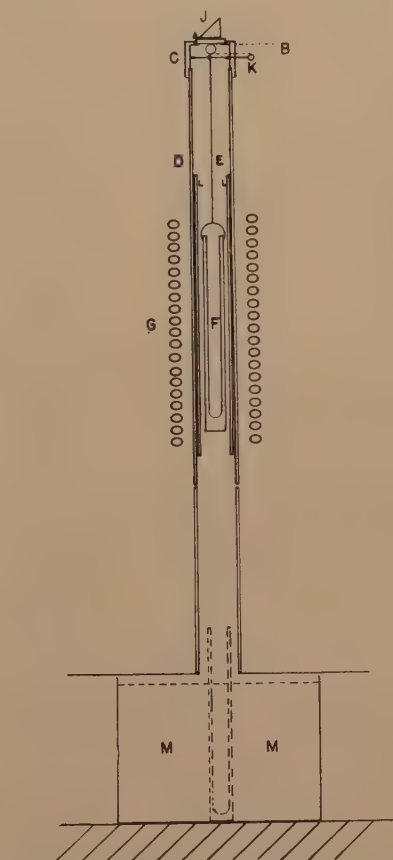


FIG. 2.—SCHEMATIC VIEW OF FURNACE FOR PREPARING SAMPLES BY WATER QUENCHING.

(30 in. long, $1\frac{1}{2}$ in. outside diameter). A brass head *C* fitted tightly over the tube. It supported the pin on which the crucible *F* was suspended and had a tube connection *B* through which the nitrogen was introduced into the furnace.

Starting with sample No. 18, prepurified nitrogen was used instead of purified tank nitrogen. Information received from the supplier indicated that the oxygen and hydrogen contents of this gas were less than 0.002 per cent.

The crucibles were machined from graphite rods of exceptional purity. Since they stood up well, only two were used in gas quenching and three in water quenching. One of the latter had been heated in vacuum at 800° to 1000°C. for about $\frac{1}{2}$ hr. to drive off any contaminants, but it was considered unnecessary to treat the others in this manner.

The copper used was special high-purity metal prepared by the method of Smart, Smith and Phillips.¹³ The electrolytic sheets were cut into long strips, cleaned with 1:1 hydrochloric acid and charged to the crucible. Starting with run No. 13, the weight charged was increased to 40 to 60 grams, which provided at least two samples for analysis. Samples No. 4 and No. 6 (gas quenched) were made by remelting continuously cast high-purity rod.

Temperatures were measured by a Leeds and Northrup disappearing-filament pyrometer sighted on the surface of the bath through the prism *J* and the sight glass *A* in the furnace head. Since the metal bath occupied only a fraction of the total height of the crucible, particularly in water quenching, black-body conditions were approached. The pyrometer was calibrated against the melting point of copper.

The charge was heated by induction. In order to raise the temperature above 1550°C. , it was found necessary to insert an alundum tube *L* as a radiation shield inside the furnace. No difficulty was then found in heating the melts to 1750°C. or higher with a power input of about 12 kilovolt-amperes.

The procedure in making a run consisted of suspending crucible and charge by the molybdenum wire *E* on the release pin *K*. Nitrogen was then turned on and allowed to flow freely out of the open end of the furnace tube. The power was then turned on and the metal melted and brought to temperature. After being held

at this temperature long enough to reach equilibrium, the crucible was dropped into the quenching bath by withdrawing the release pin.

Most samples had fairly deep pipes and clean surfaces. They were machined to slightly over $\frac{3}{8}$ -in. diameter and a length of about $1\frac{1}{4}$ in. For instance, samples 15A and 15B were machined from a cast diameter of 0.432 in. to a final diameter of 0.397 in. Care was taken to reject metal from the region of the pipe by drilling, since any loose graphite particles were likely to have collected there. After machining, the samples were carefully cleaned in hot 1:1 hydrochloric acid. They were then weighed and were ready for analysis.

Preparation by Continuous Casting.—

The equipment described by Smart, Smith and Phillips¹³ was used for making samples by the continuous casting process. The only noteworthy change in procedure was the substitution of carbon monoxide for hydrogen in the pocket that protected the bottom of the crucible from oxidation. However, 24 additional samples analyzed had been made with hydrogen, and no effect of the atmosphere in this pocket on the carbon contents of the rod was found.

After the high-purity copper was melted in the graphite crucible, it was brought to a constant temperature and held there for 20 to 30 min. Copper rod was then withdrawn through the water-cooled graphite die in the crucible bottom. This constituted an effective quench. After a sufficient length of sample had been withdrawn, the rod was stopped in the die. The temperature of the bath was then changed and it was again held for 20 to 30 min. at the new temperature before another sample was withdrawn. By repeating this procedure, any desired number of samples saturated at different temperatures could be made in succession from the same bath.

The temperature was measured by inserting a hollow graphite rod through the top of the crucible to within approximately one inch of the die. A platinum-platinum-rhodium thermocouple protected by a refractory tube was placed inside the graphite tube. By this method temperatures up to 1665°C . could be measured. Temperatures were also measured by sighting an optical pyrometer on the bottom of the hollow graphite rod. In run *A* this optical method was only partly successful, but in run *B* reliable measurements were obtained. It was not known, however, how nearly the temperatures at the bottom of the hollow graphite rod represented the actual temperatures from which the copper was quenched in the die. It is possible that any difference between the actual quenching temperature and the measured temperature varied with the temperature level.

Samples about $1\frac{1}{4}$ in. long were cut from the continuously cast rod, which had a diameter of $\frac{3}{8}$ in. These samples as a rule were not machined further but were cleaned thoroughly by severe etching with acids.

Method of Analysis

The method by which the copper samples were analyzed for carbon was based on oxidation of the carbon to carbon monoxide or dioxide and a quantitative determination of these gases. Three techniques were available for carrying this out: the classical combustion analysis for the determination of carbon in steel, the low-pressure combustion analysis and the classical vacuum-fusion method. The last named was chosen. This method had been developed for the determination of oxygen in steel. As mentioned earlier in this paper, Musatti and Ziliani¹¹ extended it successfully to the determination of oxygen in copper. Floe and Chipman¹⁴ also used this method for the analysis of oxygen in copper. These fusions were carried out

under reducing conditions in graphite crucibles. For the purposes of this investigation, it was necessary to substitute oxidizing conditions and oxide refractories. As far as the authors know, this is the first time that an oxidizing vacuum fusion has been used for analytical purposes.

In principle, the method consists of introducing the sample under vacuum into a copper bath that has a fairly high oxygen concentration. As the sample fuses into the bath any carbon present forms gaseous oxides. These gases are removed, together with any other gases that may be evolved, and are analyzed. A simplified schematic diagram of the equipment used is shown in Fig. 3. Much information on details of construction is available in a paper by Chipman and Fontana.¹⁶ In adapting the available equipment to oxidizing fusions, a furnace was used from which carbonaceous material and dust had been carefully removed. The bath was held in a small alundum crucible *D* supported by magnesia packing *E* inside a larger alundum crucible *C*.

At the start of a run, the bath consisted of copper weighing approximately 60 grams, to which 4 or 5 grams of cupric oxide had been added. The copper samples to be analyzed were placed in a glass head *A* from which they could be transferred into the funnel *B* by pushing a piece of iron with a magnet. The sleeve that guided the sample from the funnel head into the crucible was made of vitreous silica tubing.

It was possible to load and manipulate six samples in each analytical run and to reload twice without renewing the copper bath in the crucible. After three runs, the crucible became nearly filled and usually showed signs of disintegration. The crucible and bath were then replaced. A metallographic examination of several sections indicated that the copper baths even after use contained an ample supply of oxygen.

To start a run, the system was first evacuated. The bath was then melted by

induction, brought to a temperature of approximately 1400°C ., and held there for an hour or more in order to bake out any gases. The vacuum was read continuously with a thermocouple gauge.

volume *I*, which was formed by the pump on one side and the stopcock marked *I* on the other. An *n*-butyl phthalate manometer was attached to this volume and the pressure exerted by the gases could thus be

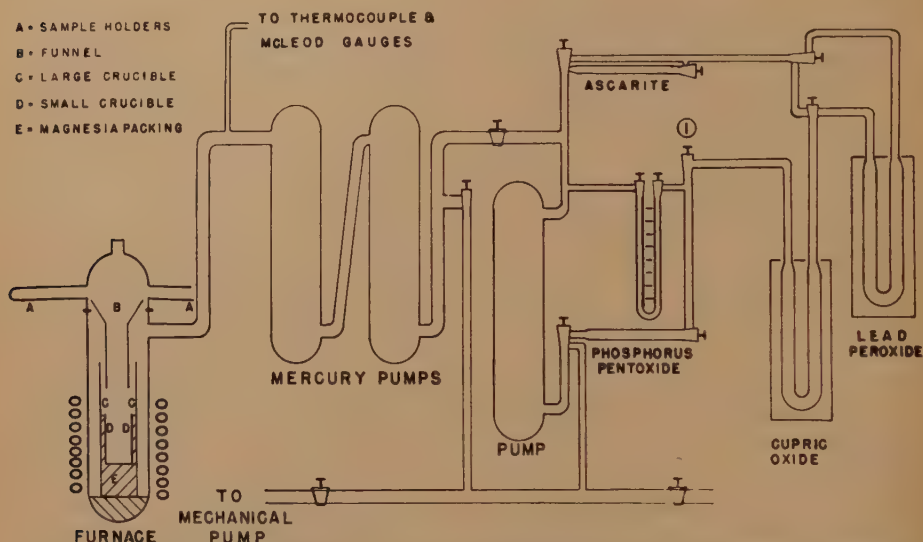


FIG. 3.—SIMPLIFIED SCHEMATIC DIAGRAM OF EQUIPMENT FOR VACUUM FUSION ANALYSIS.

After the baking out period, the power input was reduced until the temperature had fallen to about 1150°C . The amount of gas per unit time evolved at this temperature was measured in order to find the blank correction. The first sample was then introduced into the molten bath.

The samples usually melted without difficulty in 1 to 3 min. Gases were evolved as soon as the sample began to fuse and in many instances fairly large bubbles were observed breaking through the surface of the bath. The gases were pumped out by two mercury pumps in series, which transferred them to the analytical system. The gas content of most samples was evolved in 5 to 10 min. and the furnace was then shut off from the analytical system. As a rule, the blank correction was measured again after each analysis.

In the analytical system, the gases were moved by another mercury pump into

read. Since the phosphorus pentoxide tube was part of volume *I*, any water vapor present was immediately removed and the original as well as subsequent pressure readings were on a dry basis.

After the original pressure had been measured, the gases were circulated over cupric oxide at about 300°C . and brought back to volume *I*. This oxidized any hydrogen present to water vapor, which was absorbed by the phosphorus pentoxide. The decrease in pressure in this step represented the hydrogen that had escaped from the bath without oxidation.

The gases were then passed through ascarite. The decrease in pressure corresponded to the carbon dioxide present. Since the cupric oxide treatment oxidized the carbon monoxide as well as the hydrogen, the pressure change caused by passing the gases through ascarite was a measure of the total carbon in the gases. A special

treatment designed to absorb sulphur dioxide will be discussed later.

None of the samples included in Tables 2 and 3 contained hydrogen. It is believed that, owing to adsorption and desorption effects in the analytical system, the total gas evolved initially by a sample represented the true amount of carbon gases more accurately than did the pressure decrease following absorption in ascarite. The former values have been reported therefore in the tables. The difference between the two values, however, was never large. In the analysis of 24 additional samples made by continuous casting with a hydrogen atmosphere protecting the crucible bottom,

hydrogen was found to be present. This was taken into account in arriving at the carbon values.

The vacuum-fusion equipment was calibrated by admitting a known volume of dry nitrogen and recording the corresponding pressure on the manometer. In this manner volume *I* was found to be 306 c.c. Negligible changes in this volume were caused by minor glass-blowing repairs and by the fact that the amount of phosphorus pentoxide in the absorption tube varied. Naughton and Uhlig¹⁷ have directed attention to the effect of pressure and mercury-distillation rate on a volume in which a diffusion pump acts as cutoff. It is believed

TABLE 2.—Carbon Content of Quenched Samples

Sample No.	Conditions of Saturation		Results of Analysis					
	Temperature, Deg. C.	Time, Min.	Run	Sample Weight, Grams	CO ₂ Pressure Measured in Mm. of Butyl Phthalate			Carbon, Per Cent
					Total	Blank	Net	
2	1122	40	L	20.39	2.3	1.2	1.1	0.00008
3	1550	35	L	23.36	13.1	1.4	11.7	0.00077
4	1550	31	L	17.63	9.3	1.2	8.1	0.00070
5	1269	60	L-2	14.60 ^b	4.1	1.8	2.3	0.00024
6	1269	65	L-2	20.94	1.8	1.7	0.1	(0.00001)
7	1097	60	M	26.72	2.8	1.3	1.5	0.00009
8	1098	30	M	19.43	3.5	1.3	2.2	0.00017
9	1095	60	M-3	25.32	2.1	1.1	1.0	0.00006
10	1408	23	M-2	22.41	5.7	0.9	4.8	0.00033
11	1095	42	M-2	23.18	2.2	1.4	0.8	0.00005
12	1460	35	M-3	25.64	6.3	1.1	5.2	0.00031
13	1240	17	N	23.65	4.8	1.7	3.1	0.00020
14Ab	1125	43	N-1	17.22	1.5	0.8	0.7	0.00006
14Bt	1125	43	O-2	22.25	3.4	1.2	2.2	0.00015
15Ab	1450	30	N-1	19.05	3.3	1.2	2.1	0.00017
15Bt	1450	30	O-2	17.62	3.9	1.2	2.7	0.00023
16A	1192	102	P-2	24.03	7.5	1.7	5.8	0.00037
16B	1192	102	P-3	24.17	5.2	1.1	4.1	0.00026
17A	1391	75	P-2	20.26	5.1	1.1	4.0	0.00030
17B-1	1391	75	P	9.76	2.8	1.1	1.7	0.00027
17B-2	1391	75	P-3	10.98	2.6	1.2	1.4	0.00020
18A	1570	41	R-1	14.55	10.2	1.2	9.0	0.00095
18B	1570	41	R-1	12.50	8.4	0.8	7.6	0.00093
18C	1570	41	R-1	13.69	8.5	0.7	7.8	0.00087
20Ab	1727	45	S	14.00	22.7	0.8	21.9	0.00239
20Bt	1727	45	S	18.01	29.5	0.8	28.7	0.00244
21At	1735	120	S-1	16.06	34.4	1.2	33.2	0.00316
21Bb	1735	120	S-1	23.86	60.7	1.1	59.6	0.00382
26At	1516	33	T	23.34	10.8	1.6	9.2	0.00060
26Bb	1516	33	T	22.69	10.6	1.9	8.7	0.00059
27At	1516	90	T	18.17	14.9	2.8	12.1	0.00102
27Bb	1516	90	T	22.16	14.9	4.6	10.3	0.00071
28At	1727	95	T	20.94	47.2	2.1	45.1	0.00329
28Bb	1727	95	T	22.76	47.9	2.3	45.6	0.00306
29At	1730	30	T-1	20.29	56.5	3.7	52.8	0.00399
29Bb	1730	30	T-1	23.16	39.3	2.1	37.2	0.00246
30A	1275	30	U	20.57	3.4	2.2	1.1	0.00008
30B	1275	30	U	17.93	5.5	4.3	1.2	0.00010

* A "t" after the symbol specifying the sample indicates that the sample was the top section of the specimen; "b" indicates the bottom section.

A piece of presumably carbon-free tin was introduced with copper sample.

that the maximum error due to all these causes was less than 5 per cent of the pressure readings.

From the known volume, a correlation of pressure readings and carbon content of copper samples could be calculated. Based on a 10-gram sample, a pressure reading of 10 mm. corresponded to 0.00153 per cent of carbon.

RESULTS OF EXPERIMENTAL WORK

Table 2 lists the conditions of saturation and the results of the analyses of the gas-quenched and water-quenched samples. The stated time of saturation represents the period during which the sample was at the stated temperature. The sample actually was molten for a longer period, since at the beginning of a run the pyrome-

ter was calibrated by freezing and remelting of the bath. This initial period for calibration and temperature adjustment lasted 15 to 30 min. on the average.

Table 3 lists the analyses of the samples made by continuous casting. The sequence in which these samples were withdrawn from the furnace is indicated by the first numeral in the symbol signifying each sample. The letter *A* indicates the first, the letter *B* the second run.

Fig. 4 shows the carbon contents of the quenched samples as a function of temperature. Fig. 5 gives the same data for the continuously cast samples. The curves drawn to represent the results are identical in the two figures. Data shown in brackets in Tables 2 and 3 are not included in Figs. 4 and 5.

TABLE 3.—Carbon Content of Samples Made by Continuous Casting

Sample No.	Temperature of Saturation, Deg. C.	Results of Analysis					
		Run	Sample Weight, Grams	CO ₂ Pressure Measured in Mm. of Butyl Phthalate			Carbon, Per Cent
				Total	Blank	Net	
A-2-1	1650	O	16.44	24.4	1.9	22.5	0.00200
A-2-2	1650	O	15.84	24.2	1.5	22.7	0.00210
A-2-3	1650	O-I	16.95	23.8	1.4	22.4	0.00202
A-3-1	1670	O-I	15.09	27.6	1.2	26.4	0.00268
A-3-2	1670	O-I	14.16	24.5	1.2	23.3	0.00252
A-3-3	1670	R	15.40	32.8	1.6	31.2	0.00310
A-3-4	1670	R	17.11	36.1	1.0	35.1	0.00314
A-4-1	(1800) ^a	O	15.95	15.7	2.5	13.2	0.00702
A-4-2	(1800) ^a	O	14.81	72.0	3.0	69.0	0.00712
A-4-3	(1800) ^a	O-I	13.25	60.4	1.2	59.2	0.00684
A-4-4	(1800) ^a	R	10.44	52.6	0.8	51.8	(0.00482) ^b
A-5-1	1515	O-I	13.08	7.4	1.2	6.2	0.00073
A-5-2	1515	O-I	15.00	9.1	1.6	7.5	0.00076
A-5-3	1515	R	10.19	8.4	0.4	8.0	0.00076
A-6-1	1240	O	17.47	2.7	1.8	0.9	0.00008
A-6-2	1240	O	14.19	4.0	1.8	2.8	0.00030
A-6-3	1240	R	17.53	2.8	0.8	2.0	0.00017
A-7-1	1090	R	18.99	3.2	0.8	2.4	0.00010
B-1-1	1168	V	18.04	5.8	2.3	3.5	0.00030
B-2-1	1607	V	18.32	22.9	2.0	20.9	0.00175
B-2-2	1607	V-I	18.53	20.8	1.8	19.0	0.00157
B-3-1	1608	V-I	17.27	35.0	2.7	32.3	0.00286
B-3-2	1608	V-2	17.82	34.0	1.7	32.3	0.00277
B-4-1	1797	V	19.08	64.1	2.5	61.6	0.00494
B-4-2	1797	V-I	16.99	64.0	1.9	62.1	0.00550 ^c
B-4-3	1797	V-2	20.03	81.3	1.8	79.5	0.00608 ^c
B-5-1	1530	V-I	16.15	6.9	1.3	5.6	0.00053
B-5-2	1530	V-2	16.58	11.1	2.1	9.0	0.00083
B-5-3	1530	V	19.09	11.0	1.6	9.4	0.00075
B-6-1	1147	V	18.54	6.2	2.2	4.0	0.00033
B-6-2	1147	V-2	15.84	3.6	1.9	1.7	0.00016

^a Estimated temperature.

^b Time of analysis (3½ min.) was insufficient.

^c Followed by very large blank.

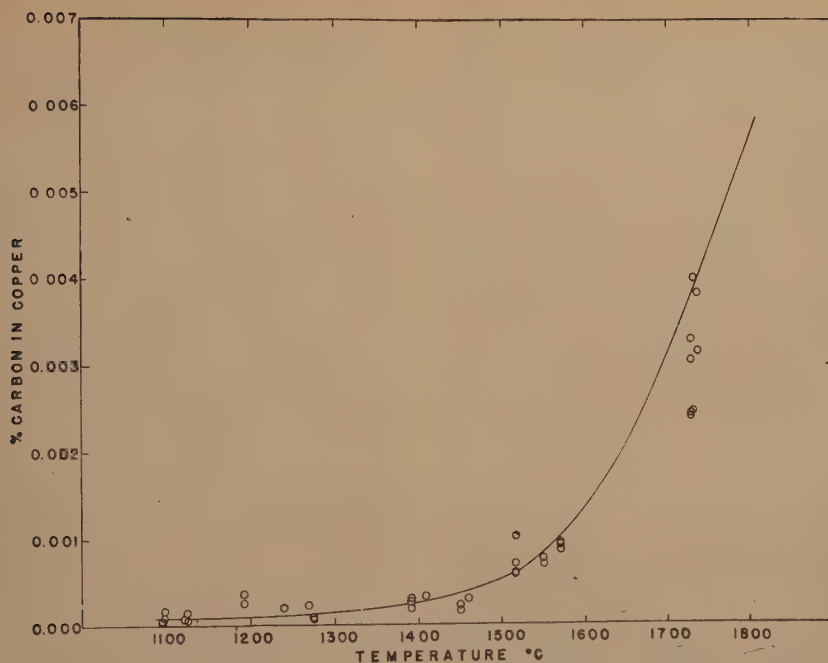


FIG. 4.—SOLUBILITY OF CARBON IN MOLTEN COPPER AS A FUNCTION OF TEMPERATURE—QUENCHED SAMPLES.

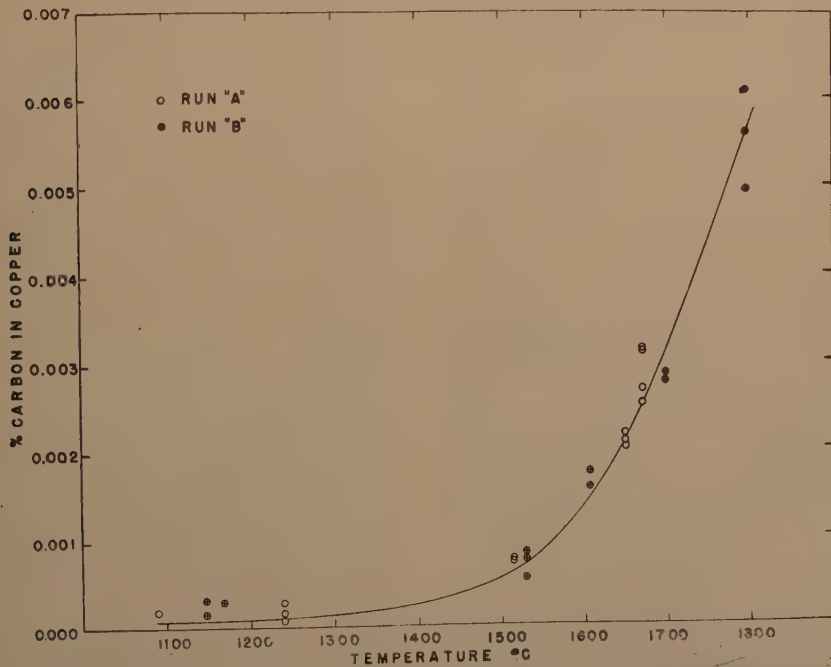


FIG. 5.—SOLUBILITY OF CARBON IN MOLTEN COPPER AS A FUNCTION OF TEMPERATURE—CONTINUOUSLY CAST SAMPLES.

DISCUSSION OF METHODS AND RESULTS

Preparation of Samples

The carbon contents of the solidified samples represented equilibrium values only if the following conditions were fulfilled: (1) the liquid bath had to be saturated with carbon, (2) this saturation amount had to be retained quantitatively in the sample during quenching, and (3) the sample had to remain free of mechanically included carbonaceous matter.

The period at which the gas and water-quenched samples were held at the saturation temperature was believed to be long enough to reach equilibrium. In addition, several samples were prepared in which saturation was accomplished by first superheating and then cooling down to the equilibrium temperature. All samples prepared in this way had large irregular pipes, were difficult to clean and gave erratic carbon results. In general these results were not as low as expected for the final saturation temperature, although some were appreciably lower than the probable carbon content for the temperature of superheating.

During analysis, the behavior of the samples prepared by superheating was different from that of the regular samples. While the gases evolved completely from the latter in 5 to 10 min., the superheated samples tended to give off gas slowly for protracted periods. Perhaps this may be explained by a difference in particle size in the precipitated carbon quenched from a solution and carbon particles rejected by supersaturation before quenching. Carbon dissolved at the superheating temperature was rejected as the temperature was lowered and may have grown into relatively large aggregates. Some of these may have been entrapped in the metal, thus giving the high results. During the analysis they may have reacted with the oxygen of the bath slowly compared with the oxidation of the dissolved carbon, which

was finely and uniformly distributed throughout the sample.

A sample prepared by superheating at 1790°C., followed by cooling slowly to solidification and then reheating to 1247°C. for 60 min., gave results higher than expected for the latter temperature, but much lower than expected for the temperature of superheating. Apparently the slow cooling and solidification eliminated most of the supersaturated carbon.

In the continuous casting process the equilibrium temperature was reached from both sides. The samples in run A represented a sequence of temperatures increasing from 1650° to about 1800°C. and then dropping to 1515°, 1240° and 1090°C. In run B the temperature sequence was 1168°, 1607°, 1698°, 1797°, 1530° and 1147°C. All of these samples gave results that indicated that the carbon dissolved at the high temperature was eliminated from the bath on cooling. This is shown in Table 3, in which the record of the samples that had been heated in contact with graphite at 1800°C. shows the carbon contents probable for the final temperature at which they were withdrawn from the bath. This proves that the continuous casting process led to saturation of these samples with carbon.

No direct method was available for checking the effectiveness of the quench as such. However, the agreement between the carbon contents of the quenched and of the continuously cast samples (Figs. 4 and 5) indicates the probability that both procedures retained the saturation values.

Aside from failure to saturate and quench the melts effectively, negative errors in carbon content could be caused by oxidation of the samples. As mentioned earlier in the paper, A. J. Phillips has called attention to the fact that the smallest trace of oxygen will remove carbon from molten copper. A few of the samples first made seemed to show some signs of superficial oxidation, which may have caused low

carbon values in some instances. However, it is felt that the use of prepurified nitrogen eliminated this source of error.

Positive errors in carbon contents could have been caused by inclusion of mechanically entrapped graphite. Actually this danger is not great if suitable precautions are taken, because of the high surface tension of liquid copper, which tends to repel graphite. The carbon contents of the quenched and of the continuously cast samples (Tables 2 and 3) are thus considered to be free from major errors caused by mechanically entrapped graphite.

The measurement of temperature was a possible source of error in preparing the samples. Optical pyrometer readings become less reliable the farther removed the observed temperature is from the calibration temperature. The temperature readings above $1500^{\circ}\text{C}.$, and especially above $1700^{\circ}\text{C}.$, may therefore have been in error by significant amounts. The inaccuracy of the temperature measurement is thus greatest in the region in which the absolute effect of temperature on solubility values is also greatest.

Method of Analysis

In order to test the method of analysis, copper samples known to be free of carbon were analyzed. High-purity electrolytic sheet was first used, and gave carbon indications of 0.00012 to 0.00069 per cent. These indications, however, were fallacious, and can be explained by the fact that the copper had been deposited in an electrolyte containing nitrate and chloride ions. Any occluded electrolyte would vaporize immediately in the vacuum fusion and the resultant volatile acidic constituents would be absorbed by ascarite and thus give the same indication as carbon dioxide. It was noticed that the gases were evolved unusually quickly in these analyses.

In a second test, electrolytic copper was first melted in an alundum crucible under

vacuum, in order to eliminate any occluded electrolyte. Copper thus prepared was satisfactory and gave no indications of carbon.

The analytical method as such was also investigated by analyzing 24 samples of continuously cast copper rod. Presumably these had been saturated with carbon at a uniform temperature, but this temperature was known only approximately to have been 1400° to $1500^{\circ}\text{C}.$ The carbon content of the last eight of these samples averaged 0.00081 per cent with a small deviation while the average of all 24 samples was slightly higher. Since these samples represented a considerable length of copper rod, it is likely that they were not all made at the same temperature, and a corresponding spread in carbon content is not surprising. Because of this uncertainty in the temperature of saturation, these data were not included in Table 3 or Fig. 5; but, assuming a temperature of $1450^{\circ}\text{C}.$, they are in reasonable agreement with the curve in Fig. 5. The main significance of these analyses lies in the fact that variations in the conditions of the analysis were found not to have any effect on the results. No correlation between such factors as time or temperature of analysis, or size of blank and the carbon contents could be found.

While the continuously cast rods were not machined as a rule, $\frac{1}{32}$ in. was removed from the diameter of two and 0.050 in. from that of one of the 24 samples mentioned. This was done in order to investigate whether the carbon concentrated in the surface layer of the rods. A comparison of the analyses of these three samples with the others in this group shows no tendency of the carbon to concentrate near the surface.

The chemical identification of carbon in the analysis was by the absorption of carbon dioxide in ascarite. The ascarite as a basic reagent would absorb any acidic gases as well as water vapor. The

only interfering constituents likely to be evolved were the volatile oxides of certain elements that may have been present as impurities.

Smart, Smith and Phillips¹³ have reported the impurity limits in their continuously cast rods. The same limits probably apply to the rods analyzed in this investigation, and they are at least a guide for the quenched samples that were made with the same types of materials. The elements to be considered are arsenic, selenium and sulphur. If they were present in the maximum amounts stated by Smart, Smith and Phillips,¹³ a carbon equivalent of 0.000069 per cent would have to be deducted. This is only a minor fraction of all but the lowest values in Tables 2 and 3.

It is questionable whether the conditions of the analysis actually allowed any interference by the oxides of selenium and arsenic. Sulphur, however, could interfere as the dioxide, or possibly the trioxide. Moreover, sulphur was the only element at all likely to be present in amounts larger than the limits set by Smart, Smith and Phillips, especially if the quality of the graphite used for crucibles was inferior. However, as mentioned before, one crucible used for water-quenched samples was heated in vacuum and showed no effect on the results obtained.

Another means of eliminating any possible interference by sulphur was the selective absorption of the dioxide. The most promising suitable reagent was lead peroxide, which Bright and Lundell¹⁸ have used at atmospheric pressure. They found that some carbon dioxide would be absorbed at 100°C. also, but that raising the temperature to about 250°C. prevented this loss. The U-tube containing the reagent prepared according to their instructions was surrounded therefore by a small resistance furnace. In testing the effectiveness of the lead peroxide as an absorbing reagent, small amounts of

commercial sulphur dioxide were admitted to the system. The absorption was found not to be quantitative but to vary from 15 to 75 per cent of the gas admitted. Some samples were prepared by melting a copper capsule made from continuously cast copper rod and containing an amount of copper sulphide calculated to introduce 0.1 per cent sulphur to the melt. When samples of this material were analyzed they gave off gases for more than $\frac{1}{2}$ hr. A partial absorption of 50 per cent or more took place when these gases were passed through the lead peroxide reagent.

It was concluded from these experiments that if any sulphur dioxide had been present in the gases evolved by the regular carbon samples, the lead peroxide reagent would have indicated its presence at least qualitatively. The lead peroxide treatment was used in a fairly large number of analyses but no indication of sulphur dioxide was found.

The analytical conditions were not favorable for the formation of any large fraction of sulphur trioxide. Although ironized asbestos was used as an absorbent for this gas in many analyses, it failed to have any effect on the results.

As an incidental result of these experiments, it was thus shown that an oxidizing vacuum fusion is not a suitable method of analysis for sulphur in copper, since the large solubility of sulphur dioxide in copper¹⁴ causes an excessively long time of gas evolution.

In evaluating the over-all accuracy of the analytical method, the blank correction must be considered. It is a relatively minor factor for carbon contents exceeding about 0.0008 per cent, but causes some uncertainty in the lower values.

SUMMARY AND CONCLUSIONS

The solubility of carbon in molten copper has been found to vary from about 0.0001 per cent at 1100°C. to 0.003 per cent at 1700°C.

Carbon dissolved even in these very small amounts can be one of the major causes of gas porosity in copper and copper-base alloys. For example, at 1200°C. the equilibrium solubility in 100 grams of copper is sufficient to form about 0.25 c.c. (STP) of carbon monoxide or dioxide if all the carbon becomes oxidized. This is equivalent to more than one cubic centimeter at the freezing point of copper. While this is a considerably smaller gas volume than the hydrogen solubility¹⁹ at the same temperature, an important difference lies in the fact that the carbon oxide gases are practically insoluble²⁰ and therefore are evolved as fast as they are formed by oxidation of the dissolved carbon.

Preliminary work on the solubility of carbon in tin bronzes shows values approximately the same as those for pure copper, so that the conclusions given above are in general applicable to these alloys.

ACKNOWLEDGMENTS

The authors are greatly indebted to Prof. John Chipman for his encouragement and interest. They also wish to express their appreciation to Prof. W. C. Schumb and Prof. J. A. Beattie for advice on experimental procedures and interpretation of results. Dr. N. J. Grant and Messrs. D. L. Guernsey and R. N. Palmer also contributed valuable suggestions and help.

Special thanks are due the American Smelting and Refining Co. for providing high-purity copper and for granting the use of continuous casting equipment. The staff of the company's Central Research Department, especially Dr. Phillips and Messrs. Smart and Smith, were very helpful.

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DISCUSSION

(S. Skowronski presiding)

J. S. SMART, JR.*—The paper that has just been presented to this group is truly an excellent contribution to the metallurgical literature. It is the type of workmanlike job that commands the respect and applause of every laboratory worker. But there is much in this work that will eventually reach the practical operator, for the real application of these findings will be classified under the subject "Gases in Metals." Everyone concerned with the casting of copper and copper-base alloys knows the importance of the complex gaseous reaction products that accompany the pouring, cooling and freezing processes. Until very recently the role of carbon in this collection of trouble makers has been given little if any consideration.

Several years ago Bolton and Smith reported serious losses of physical properties in bronze castings poured from metal that had been melted several times in an arc furnace. The difficulty was overcome by admitting air to the furnace during the melting period,

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and the circumstances strongly suggest that carbon was the offender. It should be recognized that large volumes of gases are not necessary to obtain significant damage to properties. Rather, it is the mode of distribution of the porosity that may be the determining factor, and this can be related to the mechanism of its formation. For instance, fairly good properties are often obtained from castings exhibiting a large number of spherical pores distributed at random, while specimens that appear to be much sounder suffer drastic losses of tensile strength, and particularly elongation, if the gases are preferentially located in the grain-boundary regions. Consequently, while the volumes of carbonaceous gases may be considerably smaller than those of hydrogen, their effects should not be lightly regarded.

We are indebted to Professors Bever and Floe for a set of very useful data, which undoubtedly will lend considerable assistance to the search for complete understanding of the behavior of gases in metals.

F. N. RHINES.*—The painstaking study applied by the authors to this very difficult investigation, as well as the apparently self-consistent quality of the results, inspires such confidence in their reliability as to prompt speculation on the nature of the phase diagram of the Cu-C system. Several recent investigations have shown that dry CO, free from H₂, will not produce the effect known as "hydrogen embrittlement" in tough-pitch copper, as would be expected if carbon monoxide diffused readily in solid copper. This has been interpreted to mean that the solubility of carbon in solid copper must be exceedingly small. Since oxygen, which is soluble to the extent of only a few thousandths of a per cent in solid copper, diffuses rapidly, it may be surmised that the solid solubility of carbon is very much lower, perhaps millionths of a per cent.

If this is true it would appear to indicate that the Cu-C system is of the eutectic type with the eutectic point lying near 0.0001 per cent of carbon and probably a small portion of a degree below the melting point of pure

copper. The alternative is that this is a system of the peritectic type, in which case the solubility of carbon in solid copper must be as large as, or larger than, the solubility in the liquid at the melting point. Perhaps some of the data in possession of the authors can be used to distinguish between the eutectic and peritectic possibilities on this basis.

G. P. HALLIWELL.*—I want to compliment the authors on this excellent piece of work. Probably its significance and its practical application are not fully realized.

At the present time, the Non-Ferrous Ingot Metals Institute is fostering a research at Battelle under the direction of Dr. Lorig, studying the various factors that influence the mechanical properties of a test bar. The alloy used is 85-5-5-5; that is, 85 per cent copper and 5 per cent each of tin, lead and zinc.

In a semiquantitative way, the investigators have obtained evidence on a commercial basis that may be explained by the results obtained in the paper under discussion. Metal melted in a high-frequency furnace with a siliceous lining gives slightly better results than when a clay-graphite lining is used. Perhaps Dr. Lorig would wish to comment on this.

C. H. LORIG.†—I have little to add to what Dr. Halliwell said except to state that there is some indication that the ductility of alloys of the 85-5-5-5 type prepared in a clay-graphite crucible is inferior to that of the alloys prepared in a silica crucible. The cause for the inferiority of the alloys prepared in the clay-graphite crucible has not been fully investigated, though there are strong indications that it is largely tied in with the mode of distribution of the porosity and the size and mode of distribution of the lead particles. While some early indications lead to the view that carbon in solution may be a minor influence in lowering the ductility of melts prepared in a clay-graphite crucible, further analysis of additional melts would be required to lend support to this view.

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B. H. ALEXANDER.*—The authors have pointed out that one of the most logical sources of error is in the analytical part of the vacuum-fusion apparatus, and more especially in the blank correction. Anyone who has done work with the vacuum-fusion apparatus can realize the difficulties involved. I have two questions:

1. Did the authors analyze the blank gases in any case?

2. Did they check the analytical method by introducing synthetic mixtures of gases of the composition expected?

F. R. HENSEL.†—I should like to mention one observation that we have made in the melting of special copper alloys of the age-hardening type, containing such elements as nickel and cobalt and beryllium. We have noticed that under some melting conditions, particularly if the metal is overheated and kept at a high temperature, the material after age-hardening has very erratic tensile properties and practically no elongation. When the material is fractured, it has a typical acetylene smell.

We were sure that the presence of carbon was responsible for the formation of beryllium carbides that interfered with the age-hardening characteristics of the alloys.

We also found that alloys containing nickel silicides instead of beryllides behaved in a similar manner. The curves on the solubility of carbon may throw some light on this phenomenon.

We did not approach such temperatures as 1700°C ., but we were working in the range of temperatures of 1300° to 1450° in order to dissolve special hardeners in the melt.

We believe that the surrounding gases during the melting operation have a definite effect on this carbon pickup. Additional work on this phenomenon would be of considerable interest.

P. A. BECK.‡—With reference to Dr. Hensel's remarks, I can say that in beryllium copper carbon is present in the form of beryllium carbide. This compound readily forms at very high temperatures, such as those obtaining in the electric-arc furnace, but the rate of its

formation appears to be negligible at ordinary melting temperatures.

I do not believe that the low elongation after hardening was due to the beryllium carbide.

M. B. BEVER and C. F. FLOE (authors' reply).—The authors are grateful for the discussions submitted and value particularly the confirmation of their belief that carbon in copper and copper-base alloys may be a major source of porosity in the commercial production of these materials. It is, of course, desirable to extend the investigation of the solubility of carbon to copper-base alloys, and such work is now under way.

Dr. Rhines raised the very interesting question of the probable copper-carbon phase diagram. No direct experimental observations are available that make it possible to decide whether or not this system is of the peritectic or eutectic type. However, Baukloh and Springorum²¹ found that carbon does not diffuse through solid copper and concluded that the solubility must be exceedingly small. This suggests that the copper-carbon diagram is of the eutectic type.

In reply to Mr. Alexander's questions about the method of analysis, many blanks were analyzed and found to consist essentially of carbon dioxide. The net carbon dioxide value, therefore, was determined by subtracting the blank from the total carbon dioxide. As to checks of the analytical method, no gas mixtures were employed but tank sulphur dioxide and sulphur-bearing copper were used to test the effectiveness of the lead peroxide as an absorbent. In a limited sense the calibration with nitrogen also involved a check of the analytical method.

The oxidizing vacuum-fusion analysis has promise for the determination of small amounts of carbon in ferrous materials. A study of this subject is planned. In this application a comparison will be possible between analyses of identical samples by vacuum fusion and by the classical combustion method.

In conclusion, it should be stressed that the minute amounts of carbon in copper probably do not directly affect the physical or mechanical properties to a measurable degree. The important potential effect results from the formation of insoluble carbonaceous gases if the copper is exposed to oxidizing conditions.

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²¹ *Ztsch. anorg. allg. Chem.* (1937) **230**, 315.

Effect of Phosphorus, Arsenic, Sulphur and Selenium on Some Properties of High-purity Copper

By J. S. SMART, JR.* AND A. A. SMITH, JR.* MEMBERS A.I.M.E.

(New York Meeting, October 1945)

THE controlled amounts of phosphorus, arsenic, sulphur or selenium found in commercial coppers perform a variety of highly useful functions. Indeed, a large segment of modern copper technology is essentially dependent upon the presence of one or more of these elements. Consequently, the literature contains many references to their effects but the scope is broad and has been only partly covered. New data are presented herewith directed toward a better understanding of the basic behavior of these elements in copper, with particular emphasis on the composition range 0 to 0.05 per cent.

These data are a part of a general program of research on the effects of impurities on the properties of oxygen-bearing and oxygen-free copper, other portions of which have been reported previously.^{1,2,3} Schematically, the behavior of individual elements is determined from measurements of conductivity and softening temperature,^{1,2} and the binary alloys employed are synthesized from high-purity copper in order to eliminate interference from the effects of extraneous impurities. Alloys of selected composition were first prepared in the oxygen-free form by continuously casting the melts in the

form of $\frac{3}{8}$ -in. diameter rod. Oxygen was added subsequently to portions of the alloys, either by remelting or by diffusion at 850°C. from a surface scale.

Test wires were drawn one B. and S. number per pass, using four 30-min. 600°C. anneals at 0.3125, 0.257, 0.204 and 0.162 in., and a final cold reduction of 75 per cent to 0.081 in. Oxygen-bearing slugs made by remelting were hot-rolled to $\frac{5}{16}$ in., drawn to 0.162 in., annealed for 30 min. at 600°C. and cold-drawn 75 per cent to 0.081 inch.

The alloys containing phosphorus, having been compounded very early in the program, were prepared in the form of $\frac{5}{16}$ -in. rod, and processed to wire with only the last three intermediate anneals listed above, all of these having been conducted in commercial nitrogen. In addition, the conductivity anneals on these alloys were also performed in the same atmosphere, and the small amount of oxygen present as an impurity in the gas resulted in some loss of accuracy at temperatures of 700° to 800°C., as will be shown later. Subsequently, the anneals for all oxygen-free alloys were conducted in hydrogen to prevent oxidation, and purified nitrogen was employed only for oxygen-bearing samples. All conductivity anneals were of one hour duration followed by a rapid quench in 10 per cent H₂SO₄.

EFFECT OF PHOSPHORUS

The widespread use of phosphorus as a deoxidant has resulted in universal appreci-

Manuscript received at the office of the Institute Dec. 12, 1944. Listed for New York Meeting, February 1945, which was canceled. Issued as T.P. 1807 in METALS TECHNOLOGY, September 1945.

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¹ References are at the end of the paper.

ation of the properties of the phosphorized coppers. Much of this information, acquired as a matter of commercial necessity, has never been published, but it is common knowledge that additions of phosphorus produce rapid and efficient deoxidation. If an excess of phosphorus is present over the amount needed to combine with the oxygen content, the residual quantity enters solid solution, causing, among other results, appreciable losses of conductivity. While most phosphorus-deoxidized com-

the previous work and carried out a comprehensive test program on alloys containing from 0.014 to 0.950 per cent P. Their conductivity data adequately cover the higher composition range but not the the lower range of greatest interest. Skowronski's earlier measurements⁵ are more applicable to commercial usage. Hanson, Archbutt and Ford also recognized and measured the large increase in softening temperature that attends the addition of phosphorus.

TABLE I.—*Alloys of Phosphorus and Pure Copper*

Sample No.	P, Per Cent	O ₂ , Per Cent	Hard Drawn	Conductivity, Per Cent I.A.C.S., Annealed at						Softening Temperature, Deg. C.
				300°C.	400°C.	500°C.	600°C.	700°C.	800°C.	
32M	Nil	Nil	100.05	102.3	102.3	102.3	102.45	102.3	102.25	140
23M	0.0002	Nil	100.05	102.05	102.1	102.2	102.2	102.35	102.2	182
24M	0.0008	Nil	99.55	101.7	101.8	101.8	101.8	101.75	101.8	228
18M	0.0011	Nil	99.3	101.4	101.4	101.5	101.55	101.5	101.6	238
17M	0.0059	Nil	96.35	97.0	97.95	98.0	98.1	98.3	98.45	289
30M	0.020	Nil	88.85	88.85	89.65	89.65	89.65	89.9	89.95	311
32Mo	Nil	S ^a	100.0	102.25	102.3	102.3	102.4	102.3	102.3	145
23Mo	0.0002	S	99.85	102.3	102.35	102.3	102.3	102.35	102.3	140
24Mo	0.0008	S	100.0	102.3	102.35	102.4	102.35	102.3	102.3	146
18Mo	0.0011	S	99.95	102.2	102.3	102.35	102.2	102.25	102.3	145
17Mo	0.0059	S	99.85	102.2	102.2	102.2	102.2	102.2	102.1	140
30Mo	0.020	S	100.2	101.9	102.0	102.05	102.0	102.0	102.0	133

^a Denotes saturation with oxygen by diffusion at 850°C.

mercial electrolytic coppers contain only 0.005 to 0.02 per cent P, there are at least three distinct types produced on a large-scale basis today: (1) the product containing substantially all of the phosphorus in solid solution, which is practically free from oxides of phosphorus, and in which all of the phosphorus content is available for lowering the conductivity, etc.; (2) the form in which part of the total phosphorus content is present in an oxidized condition, and the residual amount has a significant influence upon the conductivity and other properties, and, (3) the type in which the phosphorus and oxygen contents have been so judiciously balanced that the residual phosphorus content is too small to have more than a very minor effect on conductivity.

Hanson, Archbutt and Ford⁴ reviewed

In preparing the present samples by synthesis, some deviations in the intended compositions were encountered, owing to an apparent capacity for graphite to absorb phosphorus and then to release it during subsequent use. Consequently, the analyses listed in Table I are of chemical origin. Samples from both ends of each length of rod were found to be uniform.

The conductivities of the oxygen-free alloys are not uniform over the entire annealing range, as would be expected of solid solutions (Table I). However, the low values obtained from the 300°C. treatment can be readily demonstrated to be due to incomplete annealing, and the high values occurring at 700° and 800°C. represent partial loss of soluble phosphorus by the formation of an insoluble oxide. As mentioned above, these errors were derived

from the use of an impure nitrogen atmosphere, which permitted diffusion of oxygen into the test wires.

Fig. 1 presents the values representative

the volatility of this compound with the fact that the oxide can exist at high temperatures for reasonable periods of time, but, whatever its composition, it

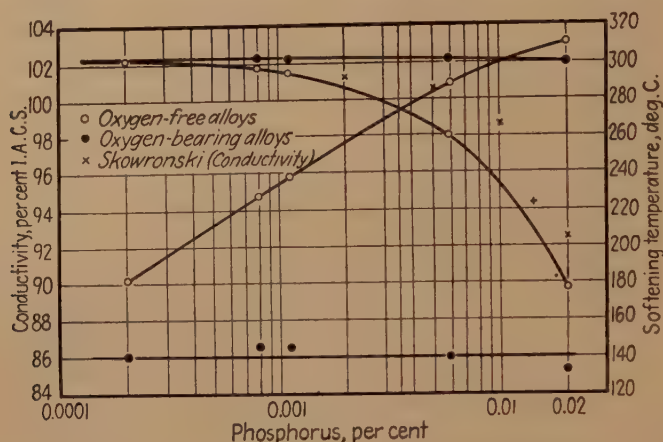


FIG. 1.—ALLOYS OF PURE COPPER AND PHOSPHORUS.

of the 500°C. anneals, together with the applicable data of the earlier work referred to. Phosphorus drastically lowers the conductivity and follows the general rule that the first additions have the largest effect. Up to at least 0.0059 per cent P each, 0.001 per cent lowers the conductivity 0.73 per cent I.A.C.S. This diminishes to an average of 0.63 per cent at 0.02 per cent P. In addition, the concomitant increases in softening temperature are of equally large order. For instance, normal phosphorized coppers containing 0.02 per cent P have a resistance to softening roughly equivalent to tough-pitch coppers containing 10 oz. per ton Ag.

As would be expected of a good deoxidant, phosphorus is completely converted to an insoluble oxide upon addition of the requisite amount of oxygen, and the very minor losses of conductivity that are noted for such alloys may be attributed to the volume occupied by the precipitated compound. The identity of the oxide formed has never been completely confirmed, but has been considered by many to be P_2O_5 . It is somewhat difficult to reconcile

probably contains a large proportion of oxygen. During the preparation of the oxygen-bearing samples by diffusion at 850°C. it was found that although an 18-hr. soak is more than adequate to saturate pure copper, the time necessary for a $\frac{5}{16}$ -in. rod containing 0.02 per cent P is between 144 and 240 hours.

EFFECT OF ARSENIC

The numerous investigations of the arsenical coppers have been comprehensively reviewed and discussed by Gregg.⁶ Quite naturally, many of the data relate to concentrations higher than those considered here. Hanson and Marryat^{7,8} and others have studied the commercial alloy range and have concluded that coppers containing 1 per cent As or more, together with normal amounts of oxygen, contain a slate-blue constituent different in appearance from Cu_2O . Smaller amounts of arsenic modify the Cu-Cu₂O eutectic, causing the familiar lamellar structure to become spheroidized with increasing arsenic content. Despite these evidences of reaction between arsenic and oxygen, Hanson and

Marryat concluded that small amounts of oxygen do not combine with arsenic to any appreciable extent if the arsenic content is less than 1 per cent.

Rhines,⁹ in his studies on the formation of subscales, has approached the question by a different method. Evidence of the precipitation of an oxide of arsenic was obtained in this manner from an alloy containing 0.03 per cent As, but the

portions were cut from the oxygen-free rods, melted in pure graphite crucibles and cast in the form of oxygen-bearing slugs, which were processed as outlined above. As previously experienced, the remelting operations resulted in further losses of arsenic, the magnitudes of which can be calculated by subtracting the compositions of the oxygen-bearing samples listed in Table 2 from their oxygen-free analogues.

TABLE 2.—*Alloys of Arsenic and Pure Copper*

Sample No.	As, Per Cent	O ₂ , Per Cent	Hard Drawn	Conductivity, Per Cent I.A.C.S., Annealed at						Softening Temperature, Deg. C.
				300°C.	400°C.	500°C.	600°C.	700°C.	800°C.	
118M	Nil	Nil	100.2	102.3	102.3	102.3	102.3	102.2	102.2	141
119M	0.0006	Nil	99.9	102.0	102.0	102.05	102.0	102.15	102.0	149
120M	0.0015	Nil	99.6	101.75	101.8	101.8	101.8	101.9	101.65	162
121M	0.0046	Nil	98.5	100.55	100.6	100.6	100.6	100.55	100.3	190
122M	0.0090	Nil	97.4	99.2	99.3	99.3	99.25	99.3	99.15	202
123M	0.0465	Nil	87.8	88.4	88.4	88.4	88.25	88.3	88.35	240
118MO	Nil	0.027	100.05	102.1	102.2	102.1	102.3	102.15	102.3	151
119MO	0.0005	0.026	99.85	101.95	102.05	102.05	102.1	102.05	102.05	150
120MO	0.0012	0.036	99.7	101.8	101.8	101.9	101.9	101.85	101.9	163
121MO	0.0043	0.026	98.5	101.05	100.65	100.7	100.65	100.65	100.7	182
122MO	0.0080	0.032	97.55	99.55	99.35	99.45	99.45	99.45	99.5	193
123MO	0.042	0.029	87.8	88.7	88.65	88.65	88.7	88.8	88.9	237

behavior of a sample containing 0.12 per cent As was uncertain. If these results are interpreted to mean that the oxidation of arsenic is only partly complete, the conclusions of earlier investigators are open to question, since their conductivity comparisons include no data obtained from oxygen-free alloys.

In preparing the present series by synthesis and carrying out the usual analytical checks for uniformity of composition, it became evident that the volatility of arsenic was responsible for significant losses during alloying, and the compositions of the oxygen-free alloys were therefore determined chemically.

Attempts were then made to prepare oxygen-bearing samples by diffusion at 850°C. These resulted in very gradual increases in conductivity with increasing time, but when, after very long periods, equilibrium had not been reached, the process was abandoned. Accordingly, fresh

The oxygen contents of these alloys were then determined by the usual process of loss in weight in hydrogen (2 hr. at 900°C.). Again, arsenic losses were encountered, and the total losses in weight (O₂ contents) of the higher arsenic alloys had to be corrected as shown in Table 2A.

TABLE 2A.—*Corrections in Weight Losses*

Sample No.	As, Per Cent	Loss in As, 2 hr. 900°C., Per Cent
119MO	0.0005	Nil
120MO	0.0012	Nil
121MO	0.0043	0.0003
122MO	0.0080	0.0023
123MO	0.042	0.0075

Since oxygen also lowers the conductivity of copper by its volume effect, the conductivity data of Table 2 have been corrected by the addition of 0.136 per cent I.A.C.S. for each 0.01 per cent O₂ present. Thus, the data for the oxygen-free and oxygen-bearing alloys are strictly com-

parable. These comparisons can be more easily made from Fig. 2, where it will be observed that the agreement between the samples, with and without oxygen, is

per cent does not react to a significant extent with the oxygen contents normal to commercial coppers.

It will be borne in mind, however, that a

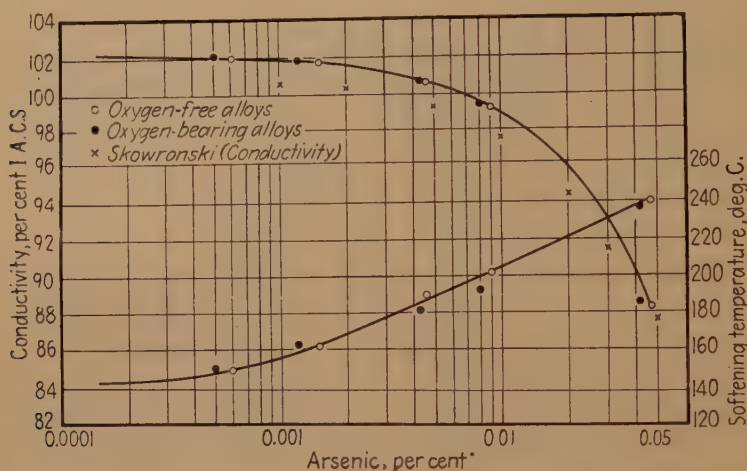


FIG. 2.—ALLOYS OF PURE COPPER AND ARSENIC.

precise with the exception of the alloys of highest arsenic content. The deviation in this case must be due to analytical errors, since if it were ascribed to the formation of an oxide of arsenic, the conductivity would have to be higher than that shown by the curve—not lower, as it is.

However, it is now known that in some cases oxide formation and precipitation occur only within a limited temperature range, and may require considerable time at temperature to progress appreciably.⁸ Therefore samples of alloy 123MO were annealed for 93 hr. at 500°C. and 92 hr. at 800°C., respectively. The treatment at 500°C. resulted in a conductivity increase of 0.95 per cent and that at 800°C. in an increase of 2.95 per cent. Upon analysis, this change in conductivity was found to be due to loss of arsenic rather than to oxide formation, and this effect explains why the previous attempts to prepare oxygen-bearing alloys by diffusion at 850°C. were unsatisfactory. Thus, it appears evident that arsenic up to 0.05

simple reaction of arsenic and oxygen is not the only possible combination that can occur in coppers of commercial purity. For while no simple oxide is formed, it has long been known that additions of lead to arsenical tough-pitch coppers will increase their conductivities very substantially.* This increase is not obtained in oxygen-free alloys, and therefore probably is due to the formation of a complex oxide.

The conductivity results of Fig. 2, being independent of oxygen content, do not differ from previously published data for the arsenical tough-pitch coppers to any notable extent. The unit effect of arsenic is at its maximum up to 0.04 per cent; in this range, each 0.001 per cent As lowers the conductivity 0.33 per cent I.A.C.S.

It is of interest to note that as arsenic is added to copper, the difference between the conductivities of the hard and annealed materials becomes less and less, finally disappearing at about 0.08 per cent As, after

* S. Skowronski: Unpublished work.

which the hard conductivity is appreciably higher than the annealed.⁶ Suggestions that this effect could be due either to coring or the presence of oxygen do not seem prob-

effect on most of their physical properties. Broniewski and Lewandowski concluded, from their curves of properties vs. sulphur content, that the solid solubility limit is

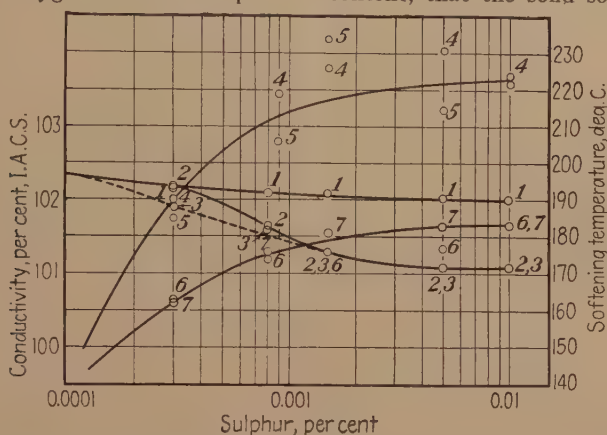


FIG. 3.—ALLOYS OF PURE COPPER AND SULPHUR.

Points 1, conductivity of oxygen-free alloys annealed 1 hour at 500°C.
 Points 2, conductivity of oxygen-free alloys annealed 1 hour at 800°C.
 Points 3, conductivity of oxygen-free alloys annealed 7 hours at 800°C.
 Points 4, softening temperature of oxygen-free alloys. Penultimate anneal 1 hour at 850°C.
 Points 5, softening temperature of oxygen-bearing alloys. Penultimate anneal 1 hour at 850°C.
 Points 6, softening temperature of oxygen-free alloys. Penultimate anneal 2 hours at 600°C.
 Points 7, softening temperature of oxygen-bearing alloys. Penultimate anneal 2 hours at 600°C.

able in view of the behavior of the present oxygen-free series, which is substantially free from both. The master alloy used in preparing the alloy series contained 0.121 per cent As and the hard and annealed conductivities were 72.7 and 72.1 per cent, respectively.

In addition to the commercially important effect of arsenic on the conductivity, increases in softening temperature also occur. While these may be considered moderate in the composition range here studied, their magnitude in the commercial alloy range is of important significance. The data herein presented confirm the general behavior indicated by the conductivity measurements.

EFFECT OF SULPHUR

The studies of Siebe¹⁰ and Broniewski and Lewandowski¹¹ indicate that the small amounts of sulphur present in the refined coppers of commerce have a very minor

less than 0.03 per cent S. Siebe's data for alloys containing 0 and 0.01 per cent S are practically identical. High amounts of sulphur are generally agreed to be deleterious to most physical properties. For very low sulphur contents, the quantities and behavior of the gaseous compounds of sulphur that escape from molten copper, under the conditions that attend the casting of the tough-pitch varieties, have evidently been considered in more detail than the effects of what remains in the solid bars. For despite the fact that sulphur is a component of all commercial coppers, its solid solubility is unknown and data concerning its behavior in the oxygen-free form are extremely scanty.

To ensure the purity of the alloys used in the present study, the master alloy was made from pure copper and Cu_2S obtained by precipitation of pure copper with H_2S . Chemical analyses made on the con-

tinuously cast rods indicated that the highly reducing conditions under which alloying took place prevented detectable losses from the intended compositions. In order to avoid such losses in the oxygen-bearing series, the oxygen was introduced into the $\frac{3}{8}$ -in. rods by diffusion for 40 hr. at 850°C. rather than by remelting. Wires were then prepared for conductivity tests by the usual procedure. The data are presented in Table 3 and Fig. 3.

It is apparent that the first 0.0003 per cent S added produces a loss in conductivity

containing 0.005 and 0.01 per cent S suffered conductivity losses of 1.2 per cent when annealed at 800°C., whereas the maximum volume effect to be expected of these amounts of sulphur in the form of insoluble Cu_2S is but 0.08 per cent.

The shape of the conductivity curve representing the 800°C. anneals given in Fig. 3 suggests that equilibrium was not reached in the one-hour period at temperature, and the same wires were therefore reannealed for an additional 6 hr. This treatment caused further losses of con-

TABLE 3.—*Alloys of Sulphur and Pure Copper*

Sample No.	Sulphur, Per Cent	O ₂ , Per Cent	Hard Drawn	Conductivity, Per Cent I.A.C.S., Annealed at						Softening Temperature, Deg. C.	
				300°C.	400°C.	500°C.	600°C.	700°C.	800°C.	2 Hr. 600°	1 Hr. 850°
136M	Nil	Nil	100.25	102.2	102.3	102.3	102.4	102.4	102.3	136	136
142M	0.0003	Nil	100.1	102.15	102.1	102.1	102.2	102.2	102.2	163	190
143M	0.0008	Nil	100.05	102.05	102.1	102.1	102.1	102.0	101.65	174	219
144M	0.0015	Nil	100.0	102.1	102.1	102.1	102.1	102.0	101.3	176	226
145M	0.0050	Nil	99.9	102.0	102.2	102.05	102.05	101.9	101.1	177	231
146M	0.0100	Nil	99.8	101.9	102.0	102.0	101.95	101.8	101.1	183	224
136MO	Nil	S*	100.2	102.2	102.25	102.3	102.3	102.35	102.3	148	153
142MO	0.0003	S	100.1	102.15	102.2	102.2	102.2	102.1	102.1	162	185
143MO	0.0008	S	100.05	102.15	102.2	102.2	102.1	101.8	101.6	176	206
144MO	0.0015	S	100.0	102.1	102.15	102.1	102.1	101.9	101.25	181	234
145MO	0.0050	S	99.8	102.0	101.8	102.0	101.8	101.6	100.95	183	215
146MO	0.0100	S	99.95	102.0	102.1	102.1	102.1	101.8	101.1	183	222

* Denotes saturation with oxygen by diffusion at 850°C.

of one or two tenths, after which the conductivity drop obtained from samples annealed at temperatures of 600°C. or lower becomes proportionately much smaller. This suggests a solid solubility of 0.0003 per cent S or less at these temperatures. On this basis the drop resulting from larger additions can be ascribed to the volume effect of the excess Cu_2S , which may be calculated as 0.08 per cent I.A.C.S. for each 0.01 per cent S present.

However, at 700° and 800°C., considerably larger losses of conductivity are obtained, and there can be little doubt that the solid solubility has increased appreciably with these increases in temperature. This is illustrated particularly well by the fact that both the alloys

ductivity for the two dilute alloys containing 0.0003 and 0.0008 per cent S, which then gave readings of 101.9 per cent and 101.6 per cent, respectively, all the others remaining unchanged. These values are presented in the dotted section of the curve of Fig. 3.

This evidence lends additional weight to the supposition that the solid solubility of sulphur is less than 0.0003 per cent at 600°C. Furthermore, the unit effect of sulphur on the conductivity within the very limited solid solubility range is high, as would be expected from its position in the periodic table relative to that of copper. The presence of oxygen has no significant effect on the results, and consequently the well-known losses of conductivity that are

experienced when commercial coppers are annealed at temperatures higher than 600°C . can be attributed in large measure to the sulphur they contain.¹²

Because of the small magnitude of the differences in conductivity that are obtained from additions of sulphur, a precise determination of its solid solubility obviously is beyond the scope of the present data. The authors do believe that the evidence is sufficiently good for a reasonable estimation, considering the total lack of information of this type, and favor solid solubilities of about 0.0002 per cent S at 600°C ., increasing with temperature to about 0.001 per cent at 700°C . and 0.002 per cent at 800°C .

Aside from their commercial importance, the determinations of softening temperature included in Table 3 are of noteworthy benefit in corroborating the interpretation placed on the conductivity measurements. This is particularly true when significance must be placed on small changes in properties, as in the present instance. Therefore, in order to take advantage of these possibilities, two sets of measurements were made, one in which the samples were prepared using four $\frac{1}{2}$ -hr. intermediate anneals at 600°C . during processing, to provide low solid solubility of sulphur, and a second group in which the solid solubility was substantially increased by appropriate heat-treatment. This was accomplished by substituting a one-hour anneal at 850°C . and a quench for the usual fourth intermediate anneal mentioned above.

The data have an unusual degree of scatter, but there is little doubt from the upper curve representing the samples quenched from 850°C . that an appreciable increase in solid solubility over that existing at 600°C . was obtained by this treatment. If the supposition that the solubility of sulphur at 600°C . is limited to about 0.0002 per cent is correct, most of the lower curve lies beyond the solution

range. Yet, the slope is fairly large up to 0.0015 per cent S. This may possibly be due to the first small amounts of excess Cu_2S that make their appearance in this composition range; the effect of certain finely dispersed secondary phases on the softening temperature is known to be significant.

The fact that a substantial difference in softening temperature resulted from the two heat-treatments given the samples containing 0.0003 per cent S confirms the conclusion previously drawn that less than this amount is soluble at 600°C . A fair conclusion seems to be that the effect of sulphur on the properties of copper is actually quite large per unit of sulphur present in solid solution, but that the extremely small solid solubility limits the total effect to moderate dimensions.

EFFECT OF SELENIUM

In 1938, C. S. Smith¹³ revived interest in the effects of selenium in copper by successfully employing up to 1.5 per cent Se for free-machining purposes. More recently the difficulties encountered in the use of South African blister coppers have led to a number of investigations in England on the effects of tellurium and bismuth, as well as selenium. Eborall¹⁴ has recently succeeded in isolating the compounds formed by copper and selenium and tellurium and by means of X-ray powder photographs identified them as Cu_2Se and Cu_2Te . No evidence of oxide formation was obtained as suggested by Rhines, who observed subscale formation in a copper containing 0.1 per cent Se. Eborall's disclosure of the existence of a liquid phase in oxygen-bearing coppers containing selenium or tellurium at 891° and 870°C ., respectively, due to the formation of ternary eutectics, is of considerable commercial importance.

Cook and Parker¹⁵ found that up to 0.04 per cent Se is not harmful to the hot-piercing properties of copper but has some

effect on the capacity to withstand cold-working, particularly in the presence of bismuth. Bailey and Hallows¹⁶ investigated various blends of South African blisters to determine the possibility of utilizing suitable mixtures for tube manufacture, but, unfortunately for the present discussion, the base materials carried both selenium and tellurium and it was not possible to evaluate their individual effects. Skowronski's conductivity data show a uniform rate of loss at 0.005 and 0.01 per cent Se where conductivity depressions of 0.8 and 1.6 per cent were noted,

tents. The brick-red deposit that sometimes is found on the walls of the reduction tube when commercial selenium-bearing coppers are so treated was conspicuously absent in the present case.

The previously described corrections for the effect of excess Cu_2O were applied to the conductivity data to permit direct comparisons with the oxygen-free values. Corrections of this type introduce an additional source of error and it is customary to observe more scatter in the data when oxygen is introduced by remelting rather than by diffusion. Making due

TABLE 4.—*Alloys of Selenium and Pure Copper*

Sample No.	Se, Per Cent	O ₂ , Per Cent	Hard Drawn	Conductivity, Per Cent I.A.C.S., Annealed at						Softening Temperature Deg. C.	
				300°C.	400°C.	500°C.	600°C.	700°C.	800°C.	2 Hr. 600°	2 Hr. 850°
208M	Pure Cu	Nil	100.1	102.3	102.3	102.2	102.35	102.25	102.3	137	
209M	0.0005	Nil	99.95	102.0	102.1	102.1	102.05	102.1	102.1	196	210
210M	0.001	Nil	99.7	101.9	102.0	102.0	101.8	101.8	101.7	208	245
211M	0.005	Nil	99.6	101.75	101.95	101.85	101.7	101.25	100.25	237	292
212M	0.01	Nil	99.5	101.6	101.9	101.9	101.7	101.1	99.55	238	303
213M	0.05	Nil	99.3	101.3	101.7	101.65	101.4	100.9	99.0	245	307
208MO	Pure Cu	0.030	100.2	102.2	102.4	102.4	102.5	102.25	102.5	137	146
209MO	0.0005	0.033	100.05	102.15	102.15	102.05	102.2	102.15	102.15	186	207
210MO	0.001	0.033	99.9	101.95	102.05	102.2	102.05	101.85	101.55	205	227
211MO	0.005	0.037	99.7	101.5	102.0	102.05	101.9	101.1	100.35	230	282
212MO	0.01	0.041	99.35	101.65	102.0	102.15	101.85	101.05	99.55	240	290
213MO	0.05	0.035	99.35	100.85	101.75	101.8	101.55	100.75	99.45	245	295

but from 0.01 to 0.05 per cent Se the additional losses are less than 0.10 per cent for each further addition of 0.01 per cent Se. This indication of limited solid solubility is confirmed by Eborall, who observed excess Cu_2Se in samples containing 0.02 per cent Se that had been quenched from 600° and 800°C.

The alloys now to be considered were synthesized from pure copper and a continuously cast master alloy in the usual way. Oxygen-bearing samples were prepared by remelting in pure graphite and pouring through air. No selenium losses were encountered in this operation nor in the samples reduced in hydrogen at 900°C. for estimation of the oxygen con-

allowance for this, it does not appear from Table 4 that there are any significant differences between the oxygen-free and the oxygen-bearing data; consequently it is concluded that appreciable oxidation of selenium does not occur within this concentration range.

With selenium as well as with sulphur, the conductivity losses are decidedly related to the annealing temperature. At 500°C. or less, the values here obtained are considerably less than those reported by Skowronski, but as the temperature approaches 800°C. the effects are of greater dimensions, and suggest appreciable increases in solid solubility in this direction. The one-hour annealing period is too short,

of course, for more than a partial approach to equilibrium conditions, and longer periods were employed to reach at least the stage where any further changes could be

for the moment that at 800°C. at least 0.01 per cent is soluble, the conductivity losses per unit of 0.001 per cent Se at compositions 0.001, 0.005 and 0.01 per

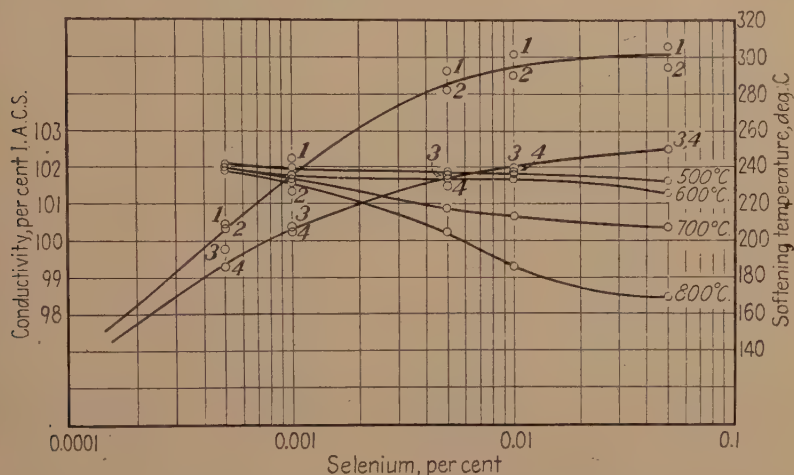


FIG. 4.—ALLOYS OF PURE COPPER AND SELENIUM.

Points 1, oxygen-free alloys. Penultimate anneal 2 hours at 850°C.
Points 2, oxygen-bearing alloys. Penultimate anneal 2 hours at 850°C.
Points 3, oxygen-free alloys. Penultimate anneal 2 hours at 600°C.
Points 4, oxygen-bearing alloys. Penultimate anneal 2 hours at 600°C.

considered to be minor. These results are reported in Table 5. Because of the greater accuracy afforded, these data, which are plotted in Fig. 4, are derived entirely from the oxygen-free alloys.

The estimation of the solid solubility of selenium is somewhat complicated by two factors that are evident from Table 5. First, it is apparent that the unit effect of soluble selenium is anything but a linear function of the composition. Assuming

cent Se are 0.6, 0.4 and 0.27 per cent I.A.C.S., respectively. In addition, the volume effect of excess selenium over that necessary to saturate the solid solution is also larger than would be expected from simple calculation, as can be seen from the following consideration of the 500°C. curve. This indicates a drop of 0.45 per cent in conductivity for a selenium content of 0.05 per cent, and this quantity is far more than is necessary to saturate the

TABLE 5.—Effect of Time and Temperature on Conductivity of Oxygen-free Alloys of Copper and Selenium
PER CENT

Sample No.	Se. Per Cent	500°C.		600°C.			700°C.		800°C.	
		1 Hr.	17 Hr.	1 Hr.	17 Hr.	33 Hr.	1 Hr.	17 Hr.	1 Hr.	6 Hr.
209M	.0005	102.1	102.1	102.05	102.0	102.0	102.1	102.0	102.1	101.9
210M	.001	102.0	102.0	101.8	101.75	101.8	101.8	101.7	101.7	101.6
211M	.005	101.85	101.9	101.7	101.75	101.7	101.25	100.9	100.25	100.25
212M	.01	101.9	101.9	101.7	101.65	101.7	101.1	100.7	99.55	99.35
213M	.05	101.65	101.65	101.4	101.4	101.4	100.9	100.4	99.0	98.5

solid solution at this temperature. Even if the amount in solid solution were neglected, and all of this amount considered insoluble,

had not equilibrium been reached in the previous treatment. However, this result indicates, at least, the validity of the

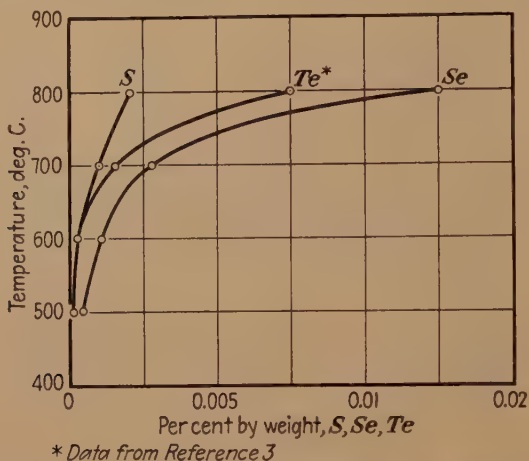


FIG. 5.—SOLID SOLUBILITY OF SULPHUR, TELLURIUM AND SELENIUM IN COPPER.

the calculated volume effect would be only 0.15 per cent.

If now the conductivities of the 0.01 and 0.05 per cent Se alloys are compared, it will be noted that up to 700°C. they differ by a constant of 0.30 per cent I.A.C.S., which represents the additional loss due to volume effect of the excess Cu_2Se in the higher alloy. At 800°C. an appreciable increase in the differential occurs; this amounts to 0.85 per cent I.A.C.S., and it can hardly be attributed to anything but solution of selenium in amounts greater than 0.01 per cent. It is recognized that failure to attain equilibrium, particularly in the sample containing 0.01 per cent Se, might have resulted in failure to obtain the lowest possible conductivity from this wire. Therefore the annealing time at 700°C. was increased to a total of 61.5 hr. The 0.05 per cent Se sample again had a conductivity of 100.4 per cent, but the conductivity of the 0.01 wire increased 0.3 per cent to 101.0. This result is anomalous, since a further decrease should have occurred at 700°C.

conductivity difference on which the solid solubility of selenium at 800°C. is presumed to be greater than 0.01 per cent. The authors make no claims for high accuracy, but feel that for most purposes the solid solubilities represented by Fig. 5 can be employed with fair success. It has not been overlooked that extrapolation of this curve to higher temperatures will result in solubilities of considerable proportions, and, if these do not actually exist, either the slope at higher temperatures can be expected to change or the present curve will need revision.

In view of the solubility behavior, the samples for the determinations of softening temperature were prepared as outlined for the sulphur-bearing coppers, in order to include conditions of high-order and low-order solubility. The data as presented in Fig. 4 show several interesting trends, among which the confirmation of the existence of a solubility change with temperature is notable. In addition, despite the very limited possibilities for solid solution at 600°C, the lower curve

indicates a progressive increase in softening temperatures over the entire composition range. This must be attributed to the effect of the dispersed Cu_2Se , as previously noted for the similar behavior of Cu_2S , and Cu_2Te ³. The curves for Cu_2Se and Cu_2Te are almost identical.

Where substantial amounts of selenium are present in soluble form, the effectiveness of the selenium additions are more pronounced. According to the upper curve, it is possible to reach rather high softening temperatures if selenium-bearing coppers are given a solution anneal at 850°C. and quenched. Selenium is intermediate in effectiveness between sulphur and tellurium, and all three behave similarly in that precipitation is rapid at even the low annealing temperatures that are used in commercial processing.

SUMMARY

1. Phosphorus enters solid solution in oxygen-free copper, resulting in major losses of conductivity and increases in softening temperature. Up to 0.0059 per cent P, the unit loss of conductivity is 0.73 per cent I.A.C.S. for each 0.001 per cent P added. Phosphorus and oxygen combine quantitatively to form an insoluble oxide.

2. Arsenic in amounts up to 0.05 per cent does not combine with oxygen and therefore is effective in both oxygen-free and tough-pitch coppers. Arsenic lowers the conductivity linearly 0.33 per cent I.A.C.S. per unit of 0.001 per cent As, within the composition range 0 to 0.01 per cent As. The softening temperature increases moderately within these limits.

3. The solid solubility of sulphur in copper increases from approximately 0.0002 per cent S at 600°C. to around 0.002 per cent at 800°C. The unit effectiveness of sulphur is high, but the total effects are curtailed by its limited solubility. Sulphur and oxygen do not combine to form an insoluble precipitate.

4. The solid solubilities of sulphur and selenium appear to be of equal magnitude at 500°C., but that of selenium increases at a much faster rate with increasing temperature, and approaches 0.015 per cent at 800°C. Selenium also does not combine with oxygen in the composition ranges investigated, and significant increases in the softening temperature can be obtained from heat-treatments that retain the soluble form. The losses of conductivity are modest.

ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance of Dr. A. J. Phillips, director of this research program. The painstaking experimental work of Mr. Stephen Mikula has been indispensable. Thanks are due also to the American Smelting and Refining Co. for permission to publish the results.

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DISCUSSION

(S. Skowronski presiding)

S. SKOWRONSKI.*—We are indebted to the authors for having furnished absolute figures on the effect of impurities upon the electrical conductivity of copper. The many experimenters who have worked along the same line started with commercial copper, and the results, therefore, were relative rather than absolute. The constants derived in this series of papers may be used for the calculation of electrical conductivity from the chemical analysis; for example, a copper refinery's monthly composite analysis of its refined copper showed: arsenic 0.0004 per cent; antimony 0.0004; selenium 0.0009; tellurium 0.0007; nickel 0.0010; oxygen 0.032; with an average conductivity of 101.31 per cent. Using the factors established by the authors, the calculated conductivity based upon this analysis was 101.24 per cent.

As pointed out by the authors, in tough-pitch copper, lead will neutralize the effect of arsenic upon the electrical conductivity. Copper containing 0.010 per cent arsenic with a conductivity of 97.6 per cent can have its conductivity increased to 100.2 by the addition

of 0.012 per cent lead. The theory advanced for this phenomenon was that lead would remove the arsenic from the solid solution as insoluble lead arsenide; however, since the authors found that in oxygen-free copper there was no increase in the conductivity when adding lead to arsenic-bearing copper, the theory will stand revision, and, as pointed out by the authors, oxygen must have a bearing on the reaction of lead with arsenic.

C. R. MARSLAND.*—The only question I should like to ask is how the oxygen determination was made on the oxygen-free copper. Nil is shown in each case, and I wonder just what it means.

J. S. SMART (author's reply).—This point was discussed in detail in the first paper of this series (see ref. 1). Briefly, the oxygen content is well below the limits of accuracy of our present analytical methods. For instance, SiO_2 and copper can be charged to the continuous casting equipment, and a silicon bronze produced due to reduction of the SiO_2 . Under these conditions we feel justified in describing the oxygen contents of these alloys as nil.

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The Effect of Phosphorus on the Properties of Gun Metal—Reducing Conditions

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(Chicago Meeting, February 1946)

MELTING procedures for most metals and alloys usually include some provision for the control of oxygen, since this element frequently has some undesirable effect on the properties of the metal or alloy concerned. In the melting of the various bronzes, this is especially true, since oxygen can be introduced into the melt in a number of ways, most of which are difficult to control.

In making bronzes from virgin materials, oxygen is usually present in the commercial grades of copper used; electrolytic fire-refined copper ingots usually contain from 0.02 to 0.05 per cent oxygen. When ingot metal or scrap bronze is used in the charge, oxides are almost always present to some degree. Under certain melting conditions and in certain types of melting equipment the atmosphere over the metal may be highly oxidizing. This, of course, may be desirable in the melting practice used, but is certain to introduce appreciable amounts of oxygen into the melt, and that may not be entirely desirable.

From the foundry viewpoint oxygen may have several harmful effects on bronzes. The formation of excessive amounts of oxides may produce drossy metal, which, in turn, means dirty castings and a potentially high rejection rate. It is claimed, too, that oxides in the metal may combine with

hydrogen to form steam and thereby produce porosity in certain of the bronzes. The presence of certain refractory oxides, such as SnO_2 , may be undesirable from the viewpoint of making machining difficult, or as possible stress-raisers in the metal matrix. It is often said that excessive oxide present in the liquid metal makes the metal run sluggishly.

Since it appears impractical to try to control the amount of oxygen introduced into the metal beyond taking the economical limit of precaution about charging dirty scrap, it would seem that control of the oxygen content of the liquid metal offers the most promising approach to this problem. This might be done by using slags, or covers, or by the use of some element or compound added to the melt to remove oxygen preferentially. Most aspects of this problem have been considered and considerable work has been done along these lines. A reconsideration of the problem is indicated, however, by the controversial nature of the evidence at hand, especially on the possibility of using a chemical deoxidizer to control the oxygen content of bronzes.

CHOICE OF DEOXIDIZER

The choice of the chemical agent selected as a deoxidizer would naturally depend first on the alloy in which it is to be used; in this particular case the alloy is Navy gun metal. In Table 1 are listed a group of elements that might be considered as deoxidizers for bronze, with some of their properties that should be considered in

This paper presents only the personal opinions of the authors and in no way reflects the official attitude of the U. S. Navy. Manuscript received at the office of the Institute Oct. 11, 1945. Issued as T.P. 1974 in METALS TECHNOLOGY, June 1946.

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making a choice.²¹ From the properties shown, aluminum, manganese, silicon, phosphorus and zinc may be selected as potential deoxidizers.

TABLE 1.—*Chemical Data on Possible Deoxidation Elements*²¹

Element	Heat of Formation per Atom Oxygen, K cal. at 18°C.	Boiling Point, Deg. C.
Ca	151.7	1240
Mg	146.0	1100
Al	127.0	1800
Si	101.3	2600
Mn	96.5	1900
P	85.0	280
Zn	83.5	907
Sn	69.0	2270

Each has some advantage and disadvantage, and phosphorus, whether it is the best deoxidizer or not, is by far the most widely used in bronze-melting practice. There is, however, considerable difference of opinion among foundrymen about the merits of phosphorus as a deoxidizer, and even among those who recommend its use there is no agreement as to how it should be used. This situation was well understood by Thews, who wrote, "... prevailing opinions concerning the use of deoxidizers, degasifiers, and fluxes are more or less erratic and diversified, the exact nature and the amount of the reagents required being more or less a matter of personal experience and inclination."¹¹

Phosphorus as a Deoxidizer

Exactly when foundrymen began thinking in terms of gun metal instead of tin bronze is not altogether clear in the literature. Some conclusions reached in work on copper-tin alloys are of interest. Rowe,² in 1924, indicated his belief that tin oxide was not reduced by phosphorus and that all phosphorus in excess of that used to remove oxygen appears as Cu_3P . Also in

1924, Vickers³ recommended the use of 15 per cent phosphor copper, 2 oz. per 100 lb., at the beginning of a heat as a deoxidizer for bronzes that contain zinc. Some general information was offered by Claus⁴ and also in an article appearing under the name "Vallishe," which recommended the use of stick phosphorus for deoxidization.⁵ Two more descriptive articles on deoxidation of bronzes appeared in 1928, one by Johnson⁶ and the other by Thews.⁷ In the following two years, Thews,^{1,9} pointed out that phosphorus, from the chemical data available, does not appear to be the most efficient deoxidizer for bronzes, but is still the most commonly used.

Falkenstoerfer¹⁰ and Parsons¹¹ studied the effect of phosphorus in red brass. Both investigators believed that phosphorus actually serves as a deoxidizer and in virgin heats, where copper is the main source of oxygen, phosphorus is necessary to remove oxides in order to make sound metal, free of inclusions. Bailey¹² wrote an excellent discussion on phosphorus in bronzes containing zinc. He declared that deoxidation with phosphorus has been said to be reversible and that an excess of 0.05 per cent phosphorus is necessary to ensure complete removal of the oxygen. Commercially, according to Bailey, an excess of 0.002 per cent phosphorus is considered adequate.

Richards¹³ stated that copper-base castings should contain only a trace, at most 0.02 per cent phosphorus, and that when more is present it can be considered an alloying element. A novel method of adding phosphorus to the metal was advocated by Claus,¹⁴ who recommended using a phosphor-copper briquette, which he had developed. The most recent paper concerning the use of phosphorus in gun metal, by George,¹⁵ suggests that phosphorus, as phosphor copper, be added at least 2 min. (preferably 5 min.) before pouring; otherwise the reaction may be incomplete and P_2O_5 , or whatever phosphorus-oxygen gas

²¹ References are at the end of the paper.

is formed, may be liberated within the casting.

Phosphorus as an Alloying Element

The influence of phosphorus in bronze on the mechanical properties (other than in phosphor bronzes) has been only cursorily examined in the past, except for a study by Dews¹⁶ on Admiralty gun metal (88-10-2). Dews' work indicated that phosphorus, up to approximately 0.05 per cent, has little effect on the mechanical properties or structure. Above 0.05 per cent phosphorus there is present fine Cu_3P and a consequent reduction in mechanical properties. Logan⁸ described a series of heats with and without additions of phosphor-copper where the use of the deoxidizer raised the average tensile strength of Admiralty metal from 38,150 to 42,570 lb. per sq. in. and the specific gravity increased from 8.57 to 8.72.

Other Effects of Phosphorus

Some research workers have contended that phosphorus in bronze acts as a degasifier and many have believed that phosphorus greatly increases the running quality (more commonly called "fluidity") of the alloy; on the other hand, many deprecate such claims.

Vickers described the action of phosphorus as one of "thinning" the metal; this, he believed, facilitated the removal of dissolved gases, since such gases could rise through the metal more easily the higher the fluidity of the metal.³ Thews⁷ took substantially the same viewpoint when he stated that phosphorus has a mechanical rather than a chemical effect.

Dews¹⁶ reported phosphorus to have a slight effect on the density of Admiralty gun metal. Falkenstoerfer¹⁰ stated that 0.03 per cent phosphorus in red brass made it flow like water; when no phosphorus was present a slag formed on the metal surface. Parsons,¹¹ also working with red brass, thought that phosphorus made the metal more fluid and protected the molten stream

during pouring. Bailey¹² implied that phosphorus did not actually form a vapor cover over the metal during pouring; he thought it more likely that a phosphate slag of high fluidity formed. George¹⁵ claimed that phosphorus would liberate any hydrogen gas present in the metal.

STATEMENT OF PROBLEM

Although the use of phosphorus as a deoxidizer in bronze manufacture is widespread, there is enough disagreement among foundrymen as to how to use it, and why it is used, to indicate that there is a scarcity of factual information about the effects of phosphorus in gun metal. This work was undertaken in an effort to supply some of this much needed information. Specifically, an attempt has been made to evaluate phosphorus as a deoxidizing agent for gun metal, to study the effect of residual phosphorus on the mechanical properties of gun metal, to determine the value of phosphorus as a degasifier, and to measure the effect of phosphorus, when used as a deoxidizer, on the running quality of gun metal.

EXPERIMENTAL PROCEDURE

The Test Casting

The test bar used in this work is shown in Fig. 1. It has been used in England by Baker¹⁷ quite successfully with gun metal, and is recommended as being especially sensitive to metal quality for this alloy. The bar is easy to mold, requires a moderate amount of metal, and is easily made ready for machining. Two bars of this type and one 6-in. bar of a one-inch square section (Fig. 2) were molded together in the flask and fed by runners from a common pouring basin. The molds were made from a synthetic sand mixture of the following composition: sand (washed silica, A.F.A. No. 61), 96.0 per cent; bentonite, 2.5; dextrine, 1.2; mogul, 0.3; water, 3.0-3.5 added. All molds were allowed to stand 24 hr. before pouring, in order to reduce the

possibility of mold moisture being a significant factor.

Melting Practice

The alloy used throughout this work was fairly close to Navy composition G; that is,



FIG. 1.—TEST BAR.

88 per cent copper, 8 tin, and 4 zinc. In order that conditions should approximate commercial practice, ingot metal, made in the Laboratory foundry from virgin materials, was used in the study.

The ingot metal was made in 225-lb. heats in a lift-coil induction furnace from electrolytic fire-refined copper, Straits tin and Horsehead zinc. The metal was cast into one-inch cylinders in sand to facilitate charging of the furnace used for pouring the test castings. No cover or deoxidizer was used in making the ingot metal. The composition was kept within Navy specifications and each was analyzed chemically.

All experimental heats were made in a 50-lb. Ajax induction furnace in magnesia crucibles. The practice consisted of melting down 50 lb. of the ingot metal, and after

the metal was molten, adding 4 oz. of charcoal to the surface of the bath. This was done in order to increase the gas content of the metal, a phenomenon observed in the Laboratory foundry as well as in many others. By having gassy metal, it was hoped



FIG. 2.—TEST CASTING.

that the effect of phosphorus as a degasifier could be determined. The weighed amount of charcoal used was enough to just cover the metal surface adequately. The charcoal was that used normally in the foundry and contained about one per cent moisture. The molten bath was brought to a temperature of approximately 1225°C ., the surface was skimmed, and the metal poured into a pre-heated clay-graphite crucible ladle in which the weighed amount of 15 per cent phosphor-copper, wrapped in copper foil, had been placed. The ladle was allowed to stand until the metal temperature had reached 1150°C . (which took from 2 to 4 min.) and two molds were then poured. By using this technique, test bars with 22 different phosphorus contents in the same base-alloy composition were obtained. All were not used, however, in all parts of the work.

Temperatures were measured by either a black-body immersion optical pyrometer or by a specially constructed chromel-alumel thermocouple connected to a sensitive millivoltmeter. Since pouring temperature is

such an important variable in this type of work, every effort was made to pour all castings at the same temperature.

Tests Conducted

From each of the test castings, the cylindrical specimens were machined to 0.875-

this work was one designed in this Laboratory (Fig. 3). Core sand was used to make the molds, which were oven dried. By such practice it was hoped that the variable of sand condition could be eliminated from the study; measurements of running quality are often difficult to reproduce because of



FIG. 3.—SPIRAL MOLD.



FIG. 4.—FLUIDITY SPIRAL.

in. diameter and 5.5-in. length. These bars were first used for measuring specific gravity by the Archimedes method. Following these measurements, standard 0.505-in. tensile specimens were machined from each bar and the tensile strength, yield strength, and elongation of each were determined. All tensile specimens were broken on a Baldwin-Southwark hydraulic testing machine and yield strengths were taken for a value at 0.10 per cent offset on the load-extension diagram.

The third bar from each casting, that of the square cross section, was machined into four standard Charpy V-notch impact specimens, which were broken at room temperature. Drillings for chemical analysis were taken from the center of the riser on the side where the bar had been cut.

"Fluidity" Tests

The running quality, or so-called "fluidity" of metals, was measured with a spiral mold similar to that developed by Saeger and Krynitsky.¹⁸ The mold used in

the number of variables involved. In these experiments the attempt was made to have the method of adding the phosphor-copper to the metal the only variable.

Gun metal was made in 200-lb. heats in the lift-coil induction furnace, from virgin materials, and cast into ingots for remelting. The ingots were then used for the charge, 100 lb. for each heat. The phosphorus was added, $2\frac{1}{2}$ oz. of 15 per cent P-Cu (approximately 0.025 per cent phosphorus) in four ways: (1) sprinkled on the metal surface; (2) sprinkled on the surface and stirred vigorously into the metal; (3) wrapped in copper foil and plunged under the surface of the metal with a bell-shaped plunger; and (4) wrapped in copper foil, placed in the bottom of a preheated clay-graphite crucible, and the metal poured over the phosphor-copper. Two heats were made with no phosphor-copper added. The metal was poured at five successively decreasing temperatures. The time interval between pouring castings was recorded, the length of the spiral was measured, and

samples for chemical analysis were taken from the constant-level pouring head. (Fig. 4.) Temperatures were measured with a black-body immersion optical pyrometer.

Micrographic examination of the various alloys showed Cu_3P to be present when the residual phosphorus was above approximately 0.06 per cent. This, of course, would

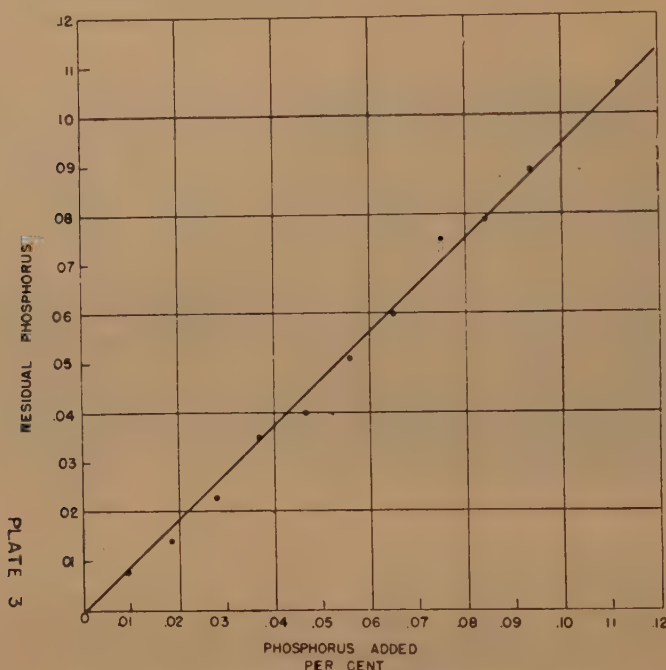


FIG. 5.—PHOSPHORUS RETAINED VS. PHOSPHORUS ADDED.

RESULTS AND DISCUSSION

Phosphorus as a Deoxidizer

From the results of the chemical analysis of the different heats containing phosphorus, the curve shown in Fig. 5 was drawn. It is apparent from this curve that most of the phosphorus added to the metal is retained. In view of this evidence, it is questionable whether or not phosphorus is acting as a deoxidizer in this alloy under the melting conditions used. Under different melting conditions, of course, phosphorus may deoxidize bronze. If the phosphorus is actually deoxidizing the metal, the chemical products of the reaction must remain in the alloy. Chemical analysis cannot usually distinguish between free and combined phosphorus.

be true only for the conditions of the experiment and cannot be considered equilibrium behavior. Below 0.06 per cent phosphorus no constituent was detected that could be identified as a phosphorus compound, and it can be inferred that the phosphorus was either in solution in the copper or present as submicroscopic particles of Cu_3P .

This behavior is not too surprising when the fact is considered that these alloys contain 4 per cent zinc, a strong deoxidizer. It is doubtful whether phosphorus will deoxidize in the presence of available zinc, although little is known about these reactions at the temperatures of liquid metal. That phosphorus will deoxidize when no zinc is present has been demonstrated in a recent paper by Pell-Walpole,¹⁰ who conducted somewhat similar experiments on

the effect of phosphorus in straight copper-tin alloys. He found, in an alloy where no zinc is present, that a certain minimum residual phosphorus content must be

phase over the metal may not be altogether correct. If such a protective blanket were present, it is doubtful that the residual phosphorus would be so high. It is known,

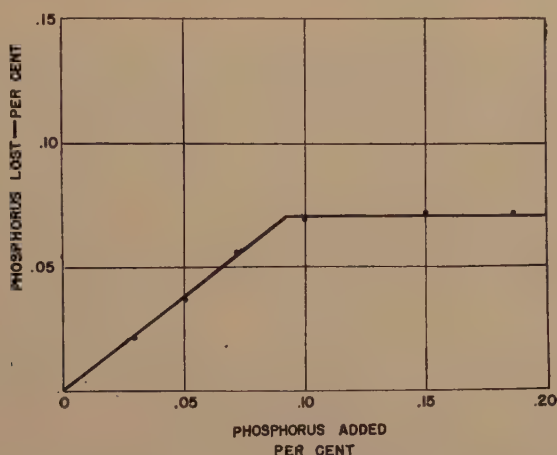


FIG. 6.—PHOSPHORUS DEOXIDATION IN A ZINC-FREE COPPER-TIN ALLOY.

reached before complete deoxidation takes place, and after that the phosphorus used up remains fairly constant. This is shown in Fig. 6, taken from the Pell-Walpole paper. Since this bronze which contained zinc retained practically all of the added

too, that the vapor pressure of P_2O_5 is high at bronze-melting temperature.²⁰ Another common belief—that phosphorus is a good deoxidizer because the products of deoxidation are gaseous and consequently easily removed—would seem to be questionable.

TABLE 2.—Data from Tests, Averaged Values

Test No.	Phosphorus Added, Per Cent	Residual Phosphorus Content, Per Cent	Specific Gravity, 20°C.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Yield Strength, 0.1 Per Cent Offset	Charpy Impact, Ft.-lb.
106	0	0	8.52	35,800	26.5	15,800	27.0
84	0.0093	0.008	8.58	39,700	31.5	16,600	30.0
86	0.0187	0.014	8.57	40,200	31.5	16,800	25.5
88	0.0280	0.023	8.51	40,100	32.5	16,500	26.5
90	0.0374	0.035	8.40	36,600	26.0	15,900	25.0
92	0.0467	0.040	8.46	37,300	24.5	16,600	25.5
94	0.0561	0.051	8.44	38,400	28.0	16,000	26.5
98	0.0750	0.075	8.29	35,450	23.5	15,600	22.0
100	0.0841	0.079	8.31	36,100	24.0	15,750	22.0
102	0.0935	0.089	8.30	33,850	22.0	15,400	23.0
104	0.112	0.106	8.26	34,300	21.5	15,550	22.0

phosphorus in these experiments, it would appear that no phosphorus deoxidation reaction occurred.

The retention of phosphorus by these alloys would seem to indicate, too, that the theory that phosphorus protects the metal during pouring by the creation of a vapor

in view of the large amounts of phosphorus retained by the metal.

Phosphorus as a Degasifier

The results of the specific gravity determinations are given in Table 2. It was found experimentally that, when com-

pletely covering the molten metal surface, charcoal can make gassy metal.²² By using identical weighed amounts of charcoal in these experiments, the effect of phosphorus

phorus is in the metal, only normal dendritic segregation can be detected and the microradiograph would be classed as average. When the residual phosphorus content

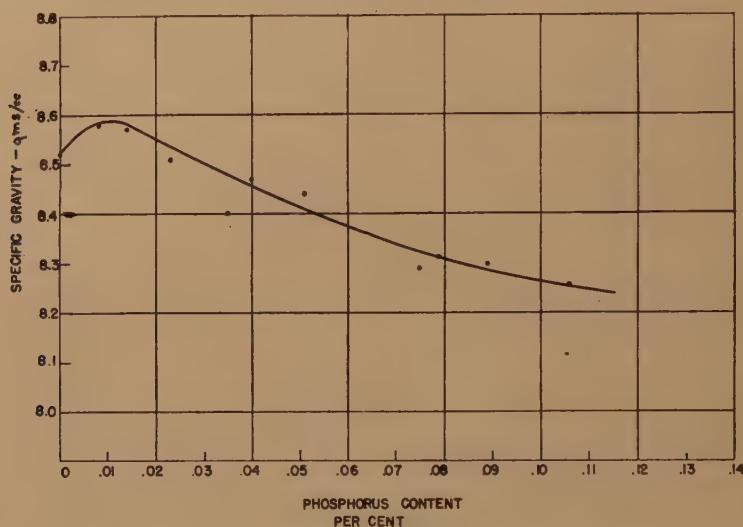


FIG. 7.—EFFECT OF RESIDUAL PHOSPHORUS ON SPECIFIC GRAVITY.

on the soundness was determined. When the data from Table 2 are plotted against the corresponding residual phosphorus content, the curve shown in Fig. 7 is obtained. It would appear from the data that up to 0.02 per cent residual phosphorus may be beneficial as far as metal soundness is concerned, but increasing the phosphorus content beyond that amount is definitely harmful.

The probable explanation of why the larger amounts of phosphorus decrease the soundness of these bronzes may lie in the effect of phosphorus on the freezing interval. It is known that substantial amounts of this element lower the solidus, particularly in the phosphor-bronzes. This increase in the solidification interval would tend to intensify the formation of interdendritic cavities and also promote greater segregation in the casting. Evidence that this is true can be seen in the microradiographs in Fig. 8. In the case where little or no phos-

is large, pronounced segregation can be observed. In the microradiographs the light areas are tin-rich and the darker are copper-rich (the tungsten radiation used is absorbed more by tin-rich than by copper-rich-material). The black areas probably represent porosity. The striated effect in the microradiograph of the bronze with the higher phosphorus content is created by the freezing first of a high-copper portion of the dendrite and the later freezing of the material high in tin (and phosphorus). Such behavior can be noted in most gun metals when the phosphorus content is much above 0.03 per cent, but in far lesser degree than shown by the microradiograph of Fig. 8.

It should be noted that the specific gravity of bronze is highly dependent on pouring temperature and that these density values will not necessarily be the same, other than relatively, for any other pouring temperature.

EFFECT OF PHOSPHORUS ON MECHANICAL PROPERTIES

The data obtained from tensile and Charpy tests are given in Table 2. The rela-

increase in properties to approximately 0.02 per cent residual phosphorus. Increased phosphorus content lowers the properties at a gradual rate. The beneficial

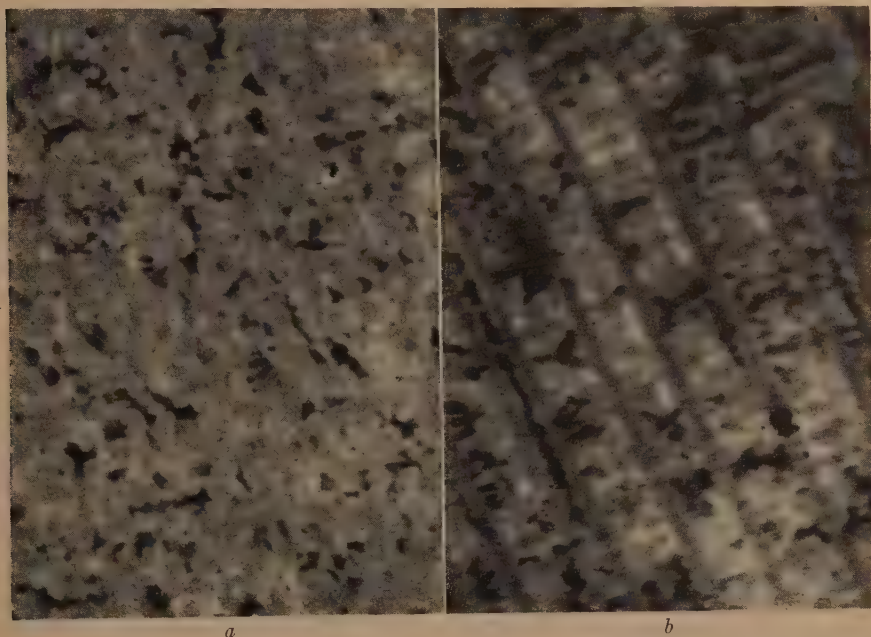


FIG. 8.—BRONZE CONTAINING PHOSPHORUS.
a, 0.008 per cent P; b, 0.112 per cent P.

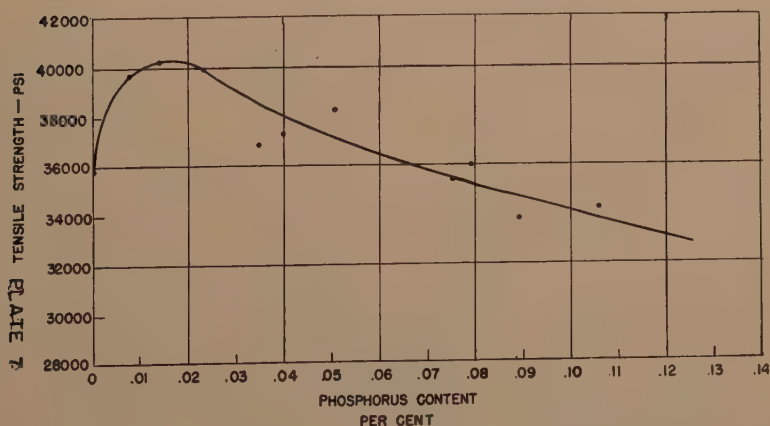


FIG. 9.—EFFECT OF RESIDUAL PHOSPHORUS ON TENSILE STRENGTH.

tionships between residual phosphorus content and the various properties are shown graphically in Figs. 9, 10, 11, and 12. The curves have similar shapes and show an

effect of phosphorus on these properties is in agreement with the recommendations of Thews⁹ and Richards,¹³ but is less than the 0.05 per cent phosphorus reported by

Dews as giving maximum properties in Admiralty gun metal. From the nature of the increases in mechanical properties it would appear that they are caused by the

Effect of Phosphorus on Running Quality

The experiments on the effect of phosphorus on the running quality or "fluidity" of gun metal were designed to determine

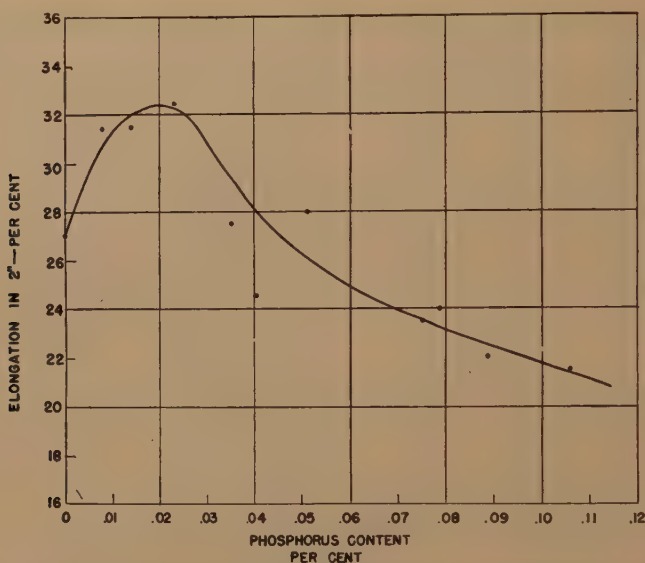


FIG. 10.—EFFECT OF RESIDUAL PHOSPHORUS ON ELONGATION.

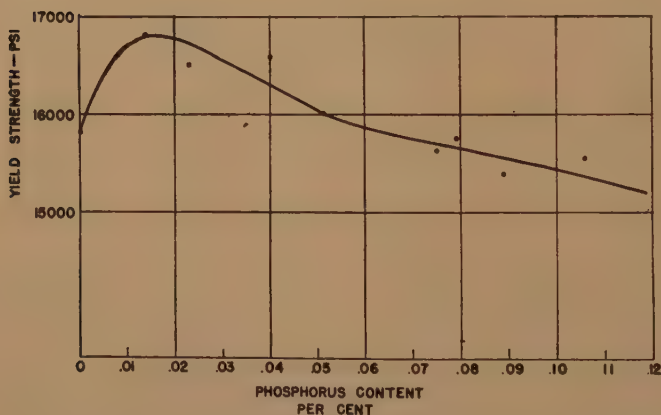


FIG. 11.—EFFECT OF RESIDUAL PHOSPHORUS ON YIELD STRENGTH.

strengthening action of these small percentages of phosphorus in solution. It is quite possible that the decline in properties with increasing phosphorus content is due to the diminished soundness.

whether or not there is any increase in the "runability" of the alloy when phosphorus is added; also, if there is any beneficial effect, to find the most efficient method of adding the phosphor-copper to the metal.

The results of the experiments are given in Table 3 and the data are plotted in Fig. 13.

From the positions of the curves in Fig. 13, it appears that phosphorus has a

the experimental technique is probably sensitive enough for comparative purposes. The relative positions of the curves for the four experiments where phosphor-copper

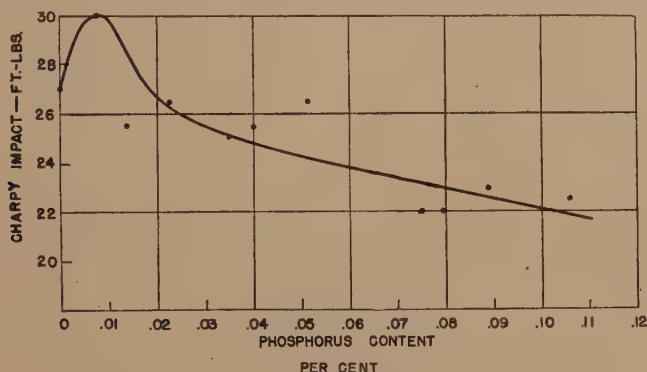


FIG. 12.—EFFECT OF RESIDUAL PHOSPHORUS ON CHARPY IMPACT.

definite beneficial effect on the running quality. The results for the experiments where no phosphor-copper was added to the metal checked satisfactorily, so that

TABLE 3.—Results of Fluidity Tests

Test No.	How P Was Added	Pouring Temperature, Deg. C.	Time between Pourings after P Addition	Spiral Length, In.	Phosphorus Content, Per Cent
F-1	Cu-P wrapped in foil plunged into bath	1150		30.5	0.024
F-2		1125		23.5	0.023
F-3		1100		19.5	0.023
F-4		1075		12.5	0.022
F-5		1045		9.5	0.020
F-6	Cu-P sprinkled on surface stirred in vigorously	1175	1:23	34.0	0.016
F-7		1150	2:22	30.5	0.018
F-8		1150	3:10	26.5	0.017
F-9		1105	4:22	22.0	0.016
F-10		1067	5:26	9.5	0.020
F-11	Cu-P sprinkled on surface	1220	:55	36.0	0.020
F-12		1185	2:15	32.0	0.019
F-13		1140	3:42	25.5	0.018
F-14		1100	5:02	19.0	0.016
F-15		1055	6:25	8.0	0.016
F-16	metal poured over Cu-P	1133	1:33	36.5	0.018
F-17		1195	3:49	34.0	0.014
F-18		1155	5:06	30.0	0.013
F-19		1120	6:08	26.0	0.012
F-20		1080	7:25	16.0	0.010
F-21	No P	1210	0	29.0	
F-22		1180	:30	23.0	
F-23		1145	2:00	19.0	
F-24		1105	3:20	14.0	
F-25		1070	4:18	12.0	
F-26	No P	1205	0	30.0	
F-27		1168	1:07	23.0	
F-28		1130	2:10	18.0	
F-29		1080	3:43	12.5	
F-30		1040	5:00	4.0	

was added in various ways indicate that pouring metal over the deoxidizer and plunging the phosphor-copper under the surface are somewhat better methods of adding the phosphorus than sprinkling it on the surface or stirring it into the metal. It should be noted, however, that this type of data has considerable scatter and exact conclusions are difficult to draw.

Some foundry metallurgists have claimed that there is no actual change in the viscosity of the metal when phosphorus is added, but that the higher fluidity is a result of lowering the liquidus temperature and consequently pouring the metal at an appreciable superheat. In view of the apparently small change in liquidus temperature caused by 0.025 per cent phosphorus, as can be seen on the Cu-P constitution diagram, this explanation seems unlikely. Other explanations of the effect of phosphorus on running quality may be found in a possible change in the surface tension of the metal, or perhaps supercooling is promoted by small residual phosphorus contents.

From the data of Table 3 it is apparent that holding the liquid metal in the ladle does not greatly alter the retained phos-

phorus content, even after six or seven minutes. There is a gradual decrease in phosphorus in the alloy, but it is small enough to be negligible. The apparent

specific gravity of the metal while greater amounts cause a gradual decrease. The decrease with larger amounts may be due to the lowering of the solidus and increase

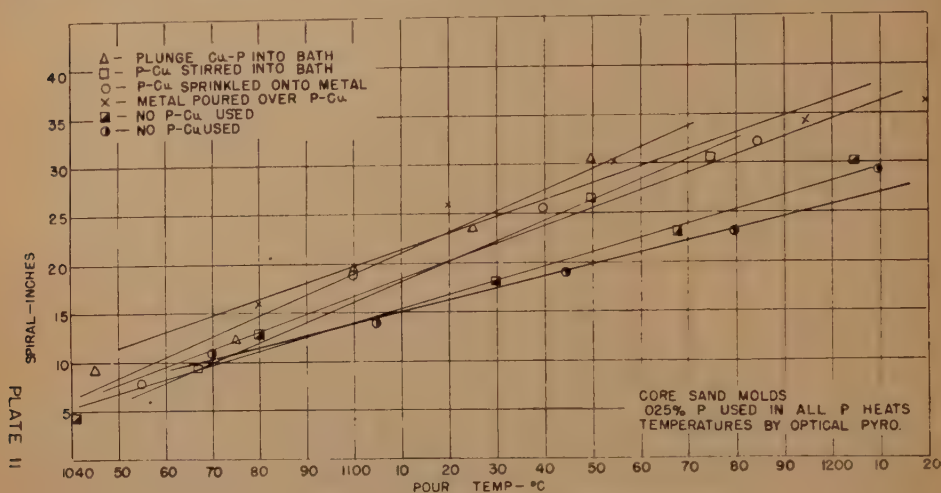


FIG. 13.—EFFECT OF PHOSPHORUS ON RUNNING QUALITY.

discrepancy in residual phosphorus content and method of adding the phosphor copper can be explained by examining the temperatures at which the spirals were poured. When the metal was poured over the deoxidizer first, it was necessary to superheat the bronze greatly (to 1270°C.). This would account for the greater reactivity of the phosphorus in this case, for instance, than when the top pouring temperature was 1150°C. In the latter instance the retained phosphorus content ran high.

SUMMARY AND CONCLUSIONS

1. It was found that most of the phosphorus added to gun metal under the melting conditions used was retained by the metal. From this evidence it seems questionable whether the phosphorus was actually serving as a deoxidizer. This seems reasonable in view of the presence of 4 per cent zinc, a strong deoxidizer in its own right.

2. Small amounts of residual phosphorus, up to 0.02 per cent, increase the

in the solidification interval. This would result in a greater formation of interdendritic cavities and probably would also cause increased segregation in the metal.

3. With up to 0.02 per cent residual phosphorus in the metal, there is considerable improvement in mechanical properties. The tensile strength, yield strength, elongation, and Charpy impact values all showed this increase. Greater amounts of phosphorus in the metal cause poorer properties. The increase in mechanical properties with small amounts of phosphorus is probably due to the strengthening action of the phosphorus in solution. The decrease in properties with larger amounts of phosphorus may be caused by the change in soundness and increased segregation.

4. From the results of the fluidity experiments, it appears that phosphorus has a definitely beneficial effect on the running quality of the metal. As might be expected, it was also found that the best method of adding the phosphorus is the one that both ensures thorough mixing and pro-

fects the phosphorus from atmospheric oxidation.

5. The results of the experiments on running quality also indicate that holding a heat of metal in a crucible for about six minutes while the temperature drops from approximately 1250° to 1050°C. does not greatly decrease the phosphorus content.

ACKNOWLEDGMENTS

The authors are grateful to the Navy Department for permission to publish this work, to Dr. F. M. Walters, Jr., for his cooperation, and to those in the Naval Research Laboratory foundry who assisted in carrying out these experiments.

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DISCUSSION

(J. H. Scaff presiding)

G. J. LeBRASSE.*—The authors should be commended on the care and details that characterize this paper, evidently the first of a contemplated series dealing with Navy G metal.

The selection of the test-bar mold has been chosen evidently for its sensitivity in showing up poor melting conditions, but have the authors poured other types of test bars such as the Webb-Webbert or Wood pattern? This question is asked because our foundry uses the Wood type of test-bar mold and a check on the last five bars pulled for foundry control shows an average of 47,250 lb. per sq. in. and 40 per cent elongation. The melting conditions were somewhat oxidizing and 0.02 per cent phosphorus was added to de-oxidize and improve fluidity.

Old records on heats made in coke furnaces also show about 45,000 tensile strength and 40 to 45 per cent elongation, and phosphorus was not added to such metal.

Although phosphorus is usually accepted by the foundry as a time-honored deoxidizer, have the authors considered lithium as a more satisfactory "degasser"?

G. P. Halliwell.†—This paper is further evidence of the ever increasing consciousness of nonferrous metallurgists to the problem of gases in metals, and of determining means to eliminate them or minimize their results.

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† Director of Research, H. Kramer and Co., Chicago, Illinois.

The recent work done by Battelle Memorial Institute for the Non-Ferrous Ingot Metal Institute on ounce metal (85 copper, 5 tin, 5 lead, 5 zinc) has shown that the bar used by the authors is not as sensitive to the gas content of the melt as other types in more common use in this country. Mechanical properties are low and are not greatly in excess of those required by A.S.T.M. Specifications, even when the melt quality is high.

The authors attribute the initial increase in the mechanical properties to the solid solution of phosphorus in the base metal. It is difficult to see how this small amount of phosphorus in solid solution could have such a marked effect on the mechanical properties. Baker and Child¹⁷ have shown that when phosphorus falls below 0.02 per cent in a 90-10 tin bronze there is a marked increase in the amount of oxygen that can be present in the equilibrium conditions. They have also shown schematically that as oxygen is reduced beyond a critical limit there is a marked increase in the amount of hydrogen that can remain in the equilibrium with the melt. Hence, any increase in phosphorus beyond 0.02 per cent, with its consequent lowering of the oxygen content, means an increase in the hydrogen and the accompanying porosity in the solid casting. It is significant that the maximum properties obtained by the authors are with a phosphorus content of the same order as obtained by Baker and Child. The increase in properties is then due to a decrease in hydrogen content and its accompanying porosity, while the decrease in properties beyond 0.02 per cent phosphorus is due to increased porosity, resulting from the high hydrogen content in equilibrium with the high phosphorus and low oxygen content in the melt.

R. A. COLTON and B. M. LORING (author's reply).—The test bar used in this work was used by Baker and Child¹⁷ in an investigation of the effect of gases in 88-10-2 gun metal and was recommended as being sensitive to gases.

¹⁷ Ref. 17, on page 169.

This sensitivity was confirmed to the author's satisfaction. The fact that the tensile properties of the alloy used here fell below those obtained with a more conventional type of bar such as the Webbert is not surprising; it should be remembered that an effort was made to produce unsound metal by using severe reducing conditions. We were interested in measuring the effect of phosphorus as a degasifier; necessarily, we had to have gassy metal with which to begin. We were not particularly interested in obtaining the best physical properties, but rather in discerning any changes in metal quality with changing phosphorus content. Had we been interested in maximum tensile properties we would have used a bar like that recommended by Mr. LeBrasse, although, with our melting conditions, it is doubtful that full properties could have been realized.

Secondary reasons for using the bar chosen were that it is well fed, eliminating shrinkage porosity as a factor in the tests; that it furnished a conveniently sized specimen for specific gravity determinations and for some damping capacity tests that are not reported in this paper.

The use of lithium to replace phosphorus as a deoxidizer and degasifier offers interesting possibilities and while that study was out of the province of this paper, it is a subject worthy of careful examination.

Mr. Halliwell's discussion of a possible reason for the increase in properties with small phosphorus contents is interesting. Since so little factual information exists on the complex equilibria involved here it is difficult to evaluate his explanations properly. It is known however that in other alloys small percentages of an element in solid solution tend to harden the metal and thereby increase physical properties. The reduction in tensile properties with higher phosphorus content appears to be caused by decreasing soundness of the metal, which may very well be due to higher hydrogen content, but may also be caused by changes in the solidification process produced by high phosphorus content.

Nickel-antimony-lead-copper Bearing Alloys

BY JOHN T. EASH,* MEMBER A.I.M.E.

(New York Meeting, October 1945)

DURING the course of the war the supply of tin in this country has steadily decreased and a continued effort has been made since the beginning of the emergency to use alloys that are either tin free or contain appreciably lower quantities of it. Even with the use of emergency materials, the tin supply has become particularly acute, and it is estimated that after recovery of the far eastern mines probably one to two years will be required before our normal annual supply is attained.

One of the major tin-consuming fields is the bronze industry. Recommendations were made several years ago by the War Production Board toward the use of bronzes of lower tin content and manganese bronze and yellow brass for the customarily used tin-bronze alloys. The substitution of 88-5-5-2 copper-nickel-tin-zinc for composition G received considerable attention before the war, and consequently this alloy and modifications of it have been adopted for some current structural and pressure castings requiring high mechanical properties.

Another of the commonly used bronzes is the 10 per cent tin, 10 per cent lead copper alloy for heavy-duty bearings. It has been known for some time that about 2.5 per cent nickel could be substituted for an equal amount of tin with retention of equivalent casting and tensile properties;

however, it was desirable that a still greater conservation of tin be made. Consequently the present paper deals with the development of an alloy of low tin content that could be used for bearings.

SELECTION OF COMPOSITION

While the final criterion of the suitability of an alloy for a bearing must of course be determined by practical applications where all the ramifications of service conditions are encountered, certain short cuts in the initial selection of compositions are necessary to avoid an extensive and time-consuming investigation. The present program has been to match certain metallurgical properties of the 80-10-10 bronze that have been shown by previous investigations to be related to good bearing qualities. Such properties as microstructure, hardness, compressive yield strength, ductility, and castability have been considered, and certain simple wear tests have been made.

Of the readily assessed characteristics desired in a good bearing alloy, one can be certain that a uniform distribution of lead is required in a leaded bronze. It has generally been found that segregation of lead is one of the chief difficulties with this type of material. Tin has a powerful effect on lead distribution, and with 10 per cent present produces a random distribution of chunky particles, such as are shown in Fig. 1. In addition, the tin bronze contains the hard $\alpha + \delta$ eutectoid constituent distributed through-

Manuscript received at the office of the Institute Jan. 5, 1945; revised Aug. 24, 1945. Issued as T.P. 1937 in METALS TECHNOLOGY, December 1945.

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out the alpha matrix, and it has an important function in the bearing.

A bearing must have reasonably good mechanical properties to withstand the

proved it slightly at 350°F. Alloying with 1 per cent antimony increased the wear resistance and the ability to withstand pounding, but decreased the toughness.

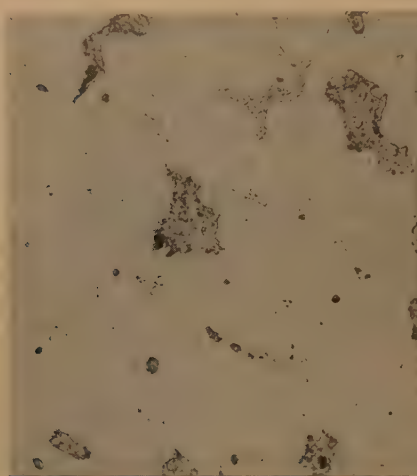


Fig. 1. 10 per cent lead, 10 per cent tin. Etched with acid ferric chloride.

Fig. 2. 10 per cent lead, 2.5 per cent nickel. Etched with ammonium peroxide.

FIGS. 1 AND 2.—MICROSTRUCTURES OF COPPER-ALLOY CASTINGS. $\times 300$.

service for which it is intended; i.e., sufficient compressive strength to support the load and adequate ductility to form a good seat. Likewise, the alloy must resist wear; so, to secure an indication of this property, wear tests of the lubricated Amsler type were made of the most promising compositions.

PREVIOUS WORK

A perusal of the literature reveals that various attempts have been made to improve the structure and properties of some of the commonly used bearing materials. After a considerable amount of work at the National Bureau of Standards on the effects of alloy additions to 80-10-10 bronze, Staples et al.¹ concluded that a 2 per cent nickel addition refined the grain and improved the lead distribution and toughness. Nickel decreased the wear resistance at room temperature but im-

proved it slightly at 350°F. Alloying with 1 per cent antimony increased the wear resistance and the ability to withstand pounding, but decreased the toughness.

Small amounts of phosphorus (0.05 per cent) were generally beneficial. Zinc had no appreciable effect. Herschman and Basil² found sulphur an aid in lead distribution in high-lead copper alloys, and after studying the effects of a wide variety of additions, they concluded that a composition having about 35 per cent lead, 0.4 per cent sulphur, 0.8 per cent zirconium and 0.6 per cent silicon had excellent wear-resistance properties.

J. Dessent³ found that the addition of 2 per cent nickel improved the homogeneity of lead in 10 per cent lead bronze.

In working with 30 per cent lead copper alloys, Wecker and Nipper^{4,5} found that segregation of lead occurred with 5 to 10 per cent tin additions, whereas with 5 per cent nickel as much as 40 per cent lead was retained. Cobalt additions were not beneficial; arsenic increased hardness and impact properties but lowered the bearing properties. They concluded that a 30 per cent lead, 2 per cent nickel, 5 per

¹ References are at the end of the paper.

cent maganese copper alloy had good frictional and shrinkage characteristics.

Guertler and Menzel⁶ found that with 2.5 per cent nickel it was possible to secure miscibility up to 50:50 lead copper.

Brinn⁷ reported that the substitution of 3 per cent nickel for 2 per cent tin and 1 per cent copper in 80-10-10 gave higher hardness and a finer structure, but the rate of wear was greater than without nickel.

Early in 1942, the Welland Iron and Brass Co., of Welland, Ontario, produced a bearing alloy containing 10 per cent lead, 8 per cent nickel, 2 per cent antimony and balance copper, but information regarding its wearing properties is not available. The present research verifies the usefulness of this type composition, as the final development is a modification of this alloy.

Dayton, Gillett and Balch⁸ recommended the use of a copper alloy containing 10 per cent lead, 2.8 per cent tin, and 2 per cent antimony as a likely substitute for 80-10-10 bronze.

These references show in general that the addition of nickel to lead-copper alloys had a favorable effect on lead distribution and would thus serve a useful purpose. A check of this indication was made by comparing the microstructures of 10 per cent lead copper melts containing 0 to 10 per cent nickel cast into bushings having $\frac{3}{16}$ -in. wall thickness and molded in green sand. The lead in the nickel-free heat was arranged in continuous intergranular films, while in the nickel-containing heats the lead films were interrupted to the extent shown in Fig. 2. There are numerous examples among alloys of the damaging effects of intergranular films in causing low strength and ductility; for example, the leaded copper alloy whose structure is shown in Fig. 2 will have only a tensile strength of about 9000 lb. per sq. in. and only 5 per cent elongation, owing to the intergranular position of the lead. In the 80-10-10 bronze, the lead is well dispersed and located in agglomerate form. Conse-

quently it seemed obvious that the structure of the latter should be duplicated as near as possible to secure the same good combination of high mechanical properties and wear resistance. While the agglomeration of lead was started in the copper-lead alloys by the nickel addition, it was incomplete. In addition, the hardness of the nickel-lead-copper alloys was about 35 Brinell as compared with 65 for the tin bronze. Obviously further improvement was needed. Consequently the effects of other alloy additions to the nickel-lead-copper base were investigated.

OUTLINE OF EXPERIMENTAL PROCEDURE

Induction-furnace melts were used in making the castings to be investigated. The order of melting was to melt down the copper and nickel together, oxidize the heat with 0.2 per cent cuprous oxide and several minutes later draw the heat back with 0.03 per cent phosphorus. This was followed by the addition of 1 per cent zinc and 10 per cent lead and any additional metals desired. A final deoxidation with 0.05 per cent phosphorus was made and the melt was then poured into green-sand molds some 200°F. above the liquidus temperatures estimated from constitutional diagrams. Temperatures of the metal bath were measured with a bare Chromel-Alumel thermocouple.

The castings employed consisted of a bushing for measuring castability, disks for wear tests and cast-to-shape tensile bars. The bushing, $2\frac{1}{2}$ in. o.d. by $\frac{3}{8}$ in. wall by 4 in. long, was cast horizontally with a heavy riser in the cope at the gated end. Experience has shown that this casting gives a good indication of the feeding characteristics of a liquid metal and its ability to produce sections free of shrinkage. The as-cast wear disks were $2\frac{5}{8}$ -in. dia. by $\frac{5}{8}$ in. thick, and were poured and fed through a central sprue. Tensile bars were cast to shape in a mold having four bars arranged horizontally.

around a square, with a riser at each corner and a central pouring sprue gated into each riser, as illustrated in previous publications.⁹ Compression specimens 0.505-in. dia. by 1 in. long were machined from the central portion of one of the bars. Samples for study of microstructure were cut from the wear disks. Examinations were made close to the wearing surface, since it is possible for the structure of leaded alloys to vary in different parts of a casting.

EFFECT OF ADDITION ELEMENTS

The effects of the various addition alloys on the hardness, fracture and microstructure are summarized in Table 1. The 0.5 per cent zirconium addition had a partial agglomerating effect on the lead, but the alloy was soft, having a hardness of only 40 Brinell because of micro shrinkage. The 0.4 per cent sulphur, 0.5 per cent zirconium alloy had a hardness of 52 Brinell and contained intergranular lead and sulphide as well as massive particles.

Bismuth and selenium did not produce globular lead. The selenium was associated with the lead, but both united to form continuous intergranular particles. Some

lead sweat and intergranular films formed in the arsenic-containing alloy.

The 30 per cent lead, 2 per cent nickel, 5 per cent manganese alloy developed by Wecker and Nipper contained massive intergranular lead. Manganese did tend to agglomerate the lead in the 10 per cent lead alloy.

From all these results, antimony appeared the most promising in dispersing the lead, and 1 per cent was quite effective. The hardness of these alloys was about 50 Brinell, which is appreciably above that of the straight nickel-lead-copper alloys. The fractures of the bushings containing 2.5 to 8 per cent nickel and 1 per cent antimony were sound, and the most satisfactory of those produced. Most of the others contained shrinkage as indicated in Table 1.

WEAR TESTS

It should be recognized that no single wear test will give an absolute measure of wear resistance and any test will give only a comparison between materials under certain specific conditions. Consequently, when conducting wear tests in the laboratory, the question invariably arises regard-

TABLE 1.—*Effect of Alloy Additions on 10 Per Cent Lead Copper*

Composition, Per Cent*			Brinell Hardness Number	Lead in Microstructure	Fracture of Bushing
Pb	Ni	Other			
10		0.5Zr	40	Some agglomerate lead; some grain boundary lead	Considerable shrinkage
10		0.5Ca		Porous	Shrinkage and gas porosity
10		0.5Li			
10		0.4S	52	Intergranular lead and sulphide. Massive particles	Shrinkage and gas porosity
30	2	0.5Zr	42	Massive intergranular lead	Much dross
10	5	1Mn	52	Few lead particles	Lead sweat
10	5	0.5Mn	50	Uniform distribution of agglomerate lead	Heavy lead sweat
10	5	1Sb	50	Lead films and agglomerate lead	Lead sweat—slight shrinkage
10	5	1Bi	40	Lead films	Lead sweat—slight shrinkage
10	5	1Se	45	Massive intergranular lead and selenide	Slight lead sweat and shrinkage
10	2.5	1Sb	45	Uniform distribution of agglomerate lead	Good
10	5	1Sb	51	Uniform distribution of agglomerate lead	Good
10	8	1Sb	50	Uniform distribution of small lead particles	Good

* Calculated.

ing the interpretation of the results and their adaptability to practice. Fortunately, in their work at the Bureau of Standards, Herschman and Basil^{2,10} found that Amsler

and in another they had lead-copper bearings tested at Wright Field in aircraft motors. With these experiences as a background, the present investigation was

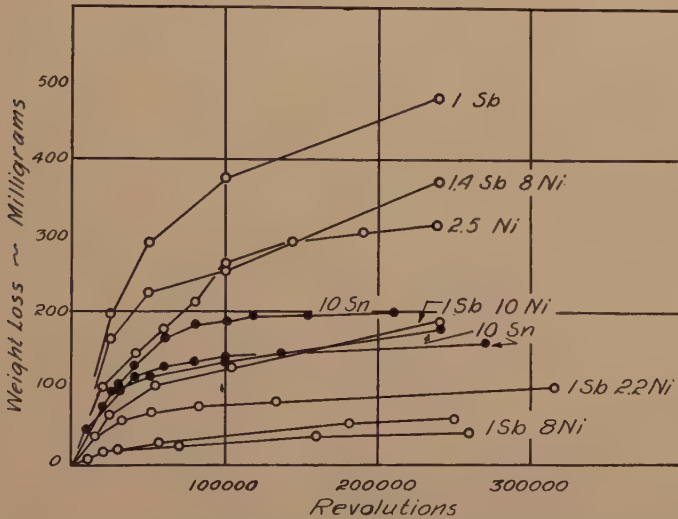


FIG. 3.—EFFECT OF COMPOSITION ON WEAR OF 10 PER CENT LEAD COPPER.

wear tests enabled them to make a selection of bearing compositions that showed up equally well in actual service conditions. In one case they worked with white-metal bearings and tested them in army trucks,

patterned on Amsler wear tests conducted in a similar manner.

This test employed a bearing-metal disk and a steel disk rotating against one another on their peripheries under a load of

TABLE 2.—Properties of Bearing Alloys

Composition, Per Cent ^a				Wear Test, 240,000 Revolutions, Weight Loss, Mg.	Brinell Hardness Number	Tensile Properties			Compression Yield, 0.5 Per Cent Compression under Load
						Ultimate, Lb. per Sq. In.	Yield, 0.5 Per Cent Extension under Load, Lb. per Sq. In.	Elongation, Per Cent	
Pb	Ni	Sb	Sn						
9.81 (10)			(10) ^b	180	67	35,300	17,600	18	19,700
(10)	(2.5)			314	34	9,600	4,575	5	
(10)		(1)		481	45	14,125	8,075	5	
10.6	2.2	0.96		95	46	11,580	9,250	3	13,550
9.0	8.0	0.96		50	53	20,140	13,250	6	
(10)	(10)	(1)		188	52	21,710	11,450	9	
9.6	8.1	1.4		372	60	25,000	13,000	9	
8.3	7.7	0.99	1.09	125	63	23,675	14,750	6	18,325
10.9	7.7	0.85	2.86	43	71	28,200	21,300	4	22,875
10.3	7.3	0.88	5.00	70	87	35,050	28,250	2	28,975

^a Alloys also contain 1 per cent zinc; balance copper.

^b Parentheses indicate calculated composition.

12 lb. To provide mild lubrication, a well of kerosene was placed under the bronze disk, so that the bearing dipped continually into the liquid and subsequently carried

any abrasive. The disks were thoroughly cleaned and weighed before each test and periodically during the run.

The standard of comparison has been the

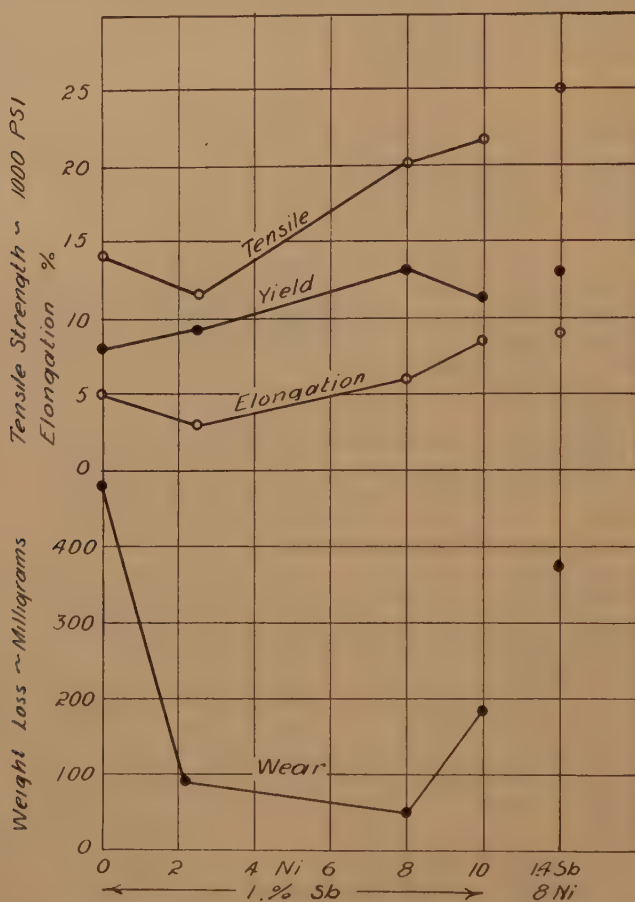


FIG. 4.—EFFECT OF NICKEL ON 10 PER CENT LEAD COPPER.

it up over the steel, which was S.A.E. 3140 heat-treated to 330 Brinell. The bronze disk rotated at 440 r.p.m. and the steel disk about 10 per cent slower in the opposite direction, to provide the maximum amount of slip. In preparing the test pieces, 2.325-in. dia. by 0.394 in. thick, the steel disks were given a fine grind finish and the bronze specimens were given a fine machine finish, to avoid including

80 copper, 10 tin, 10 lead alloy, and during the course of the investigation three separate runs were made on two specimens of this analysis. The three curves are shown in Fig. 3; they agree quite well, and the maximum weight loss was about 200 milligrams.

Upon considering in detail the wear data given in Table 2 and illustrated in Fig. 3, it is noted that 10 per cent lead copper with 1 per cent antimony or 2.5 per cent nickel

alone was inferior to 80-10-10. Not until 2.2 to 10 per cent nickel and 1 per cent antimony were added together did the wear improve substantially; with 2.2

0.9 to 1.4 kg. cm. Generally the materials of higher wear resistance developed lower torque.

From the standpoint of wear resistance

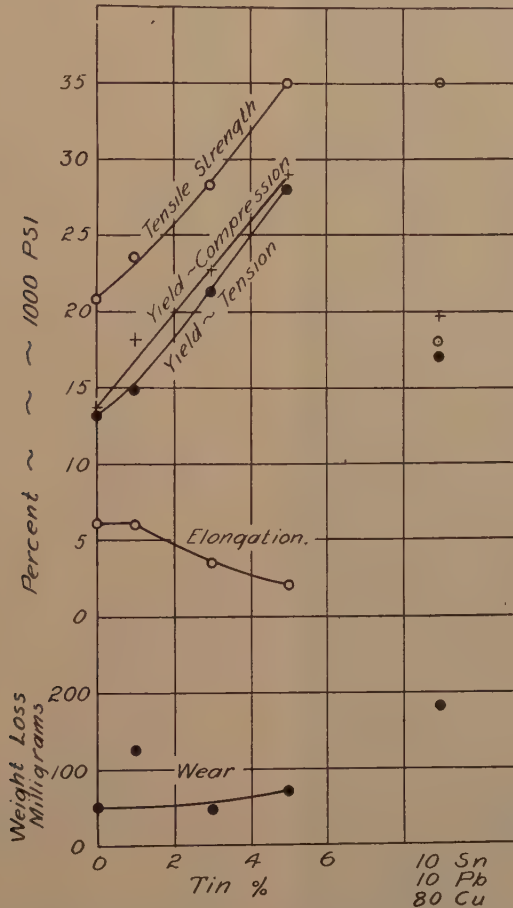
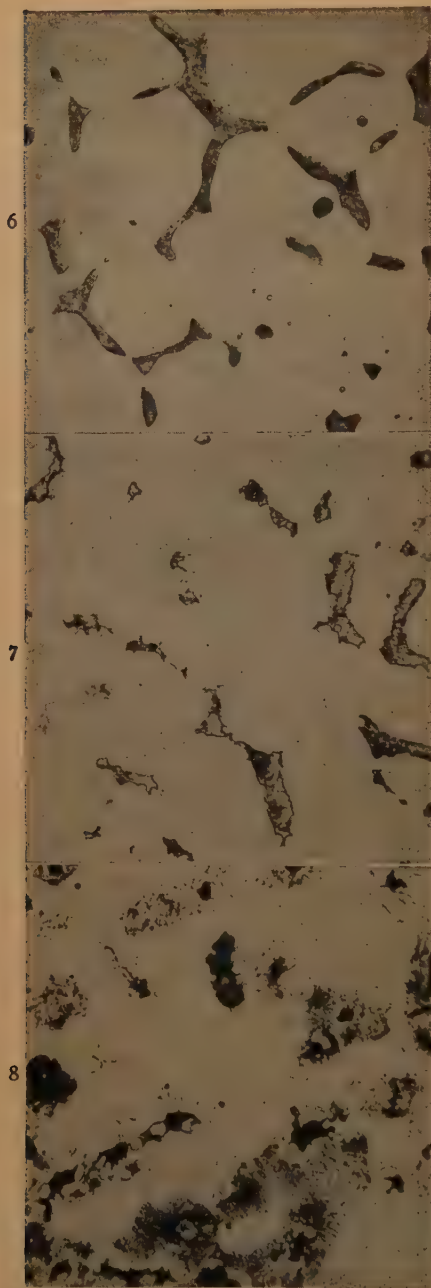


FIG. 5.—EFFECT OF TIN ON 10 PER CENT LEAD, 8 PER CENT NICKEL, 1 PER CENT ANTIMONY COPPER.

to 8 per cent nickel, wear resistance superior to 80-10-10 was obtained and at the 10 per cent nickel level the wear was equal. Raising the antimony to 1.4 per cent caused an increase in the wear loss; it appears that an addition of 1 per cent is preferable.

The wear of the mating steel disk in every case was extremely low, so that it need not be considered. The torque developed was also very low, being only

alone, the bearing containing 2.2 per cent nickel, 1 per cent antimony, 10 per cent lead would be superior to 80-10-10; however, consideration of mechanical properties leads one to select a higher nickel content, as shown in Fig. 4. The addition of nickel increased the yield strength of the antimony bronze, so that with 8 per cent nickel, 1 per cent antimony, 10 per cent lead, values were obtained that were about 70 per cent those obtained with the



FIGS. 6-8.—MICROSTRUCTURES OF COPPER-ALLOY CASTINGS. $\times 300$.

Etched with ammonium peroxide.

Fig. 6. 10 per cent lead, 1 per cent antimony.

Fig. 7. 10 per cent lead, 8 per cent nickel, 1 per cent antimony.

Fig. 8. 10 per cent lead, 8 per cent nickel, 1 per cent antimony, 3 per cent tin.

10 per cent tin 10 per cent lead bronze. Increasing the nickel and antimony still further was effective in raising the tensile strength, but, as mentioned before, was detrimental to the wear resistance.

While this material undoubtedly would find use in applications requiring excellent wear resistance, limitations would be imposed by the sacrifice in yield strength. Consequently, to bolster this weakness, additions of 1 to 5 per cent tin were made and the results given in Fig. 5 were obtained. The tensile and yield strengths of the nickel alloy increased directly with tin additions up to 5 per cent and still maintained excellent wearing properties; however, the ductility became lower. The yield in compression also increased with the tin content.

It is concluded that in order to match the yield strength of the 80-10-10 bronze in either tension or compression, approximately 2 per cent tin must be added to the 8 per cent nickel, 10 per cent lead, 1 per cent antimony composition. Although the ductility is less, it is sufficient for many bearing applications, and since the wear resistance of the new alloy is superior to the older bearing alloy, it should find its place in industry.

MICROSTRUCTURE

In the 10 per cent lead, 2.5 per cent nickel copper alloy, the intergranular formation of the lead was partially disrupted (Fig. 2) and with 1 per cent antimony alone, the dispersion of the lead had proceeded still further (Fig. 6). When the two metals were added in combination, further change occurred. The lead was more finely dispersed and a new phase appeared, which increased with the nickel content (Fig. 7). The new phase was probably a copper-nickel-antimony compound containing some lead. The copper-antimony and nickel-antimony systems are somewhat similar in that both copper and nickel retain about 8 per cent antimony in solid solution and above this amount form compounds. Apparently the addition

of nickel reduced the solubility of antimony in copper and caused the precipitation of the compound. It is also possible that the new phase contained some lead.

since castings from both melts had high rates of wear. The microstructure showed that superheating promoted the formation of intergranular lead films (Fig. 10),

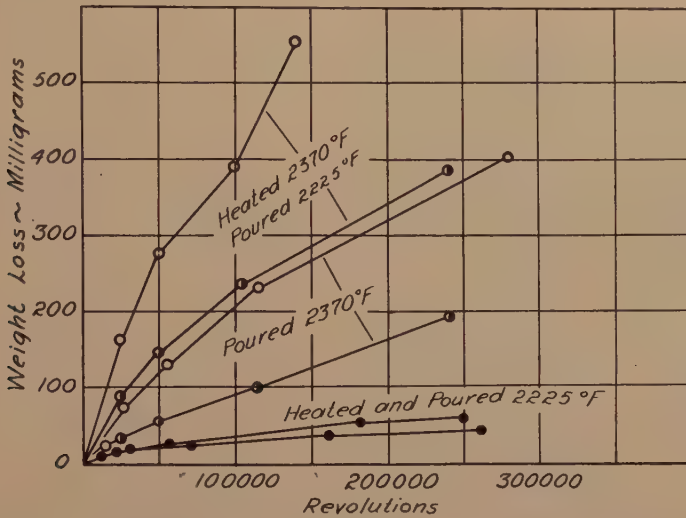


FIG. 9.—EFFECT OF SUPERHEATING ON WEAR OF 10 PER CENT LEAD, 8 PER CENT NICKEL, 1 PER CENT ANTIMONY COPPER.

The addition of tin resulted in the formation of finely dispersed theta, which appears gray in Fig. 8. This constituent precipitated from solid solution during cooling and was located in the interdendritic areas of high tin content. Apparently this cored structure was the reason for the decrease in ductility.

EFFECT OF MELTING TEMPERATURE

In order to put the new alloy into practice it was necessary to determine how it would be affected by some of the usual production variables. Since a very common one would be melting temperature, two melts of 8 per cent nickel, 1 per cent antimony, 10 per cent lead, balance copper were heated to 2370°F., which was 150°F. above the normal level. Part of each was cast into disks at the high temperature and the remainder was then cooled to the normal temperature and poured. It is evident from Fig. 9 that superheating of this alloy is to be avoided,



FIG. 10.—CAST ALLOY, 10 PER CENT LEAD, 8 PER CENT NICKEL, 1 PER CENT ANTIMONY COPPER. $\times 300$.

Superheated to 2370°F. during melting. Etched with acid ferric chloride.

which undoubtedly contributed to the poorer wear resistance. Heating temperatures during melting, consequently,

should be limited to about 2250°F. and the pouring temperature determined by the section being cast.

inferior to the sand castings. Chilling produced a very fine microstructure (Fig. 12). Apparently a uniform distribu-

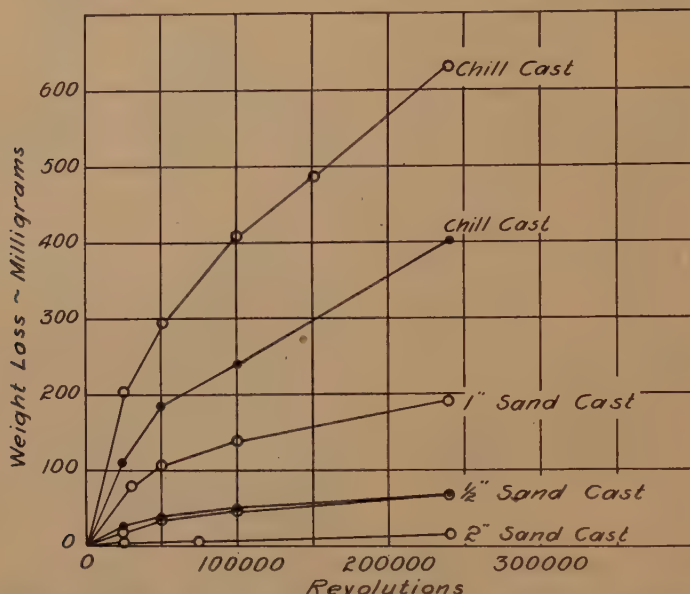


FIG. 11.—EFFECT OF CHILL AND SECTION SIZE ON WEAR OF 10 PER CENT LEAD, 8 PER CENT NICKEL, 1 PER CENT ANTIMONY COPPER

EFFECT OF SECTION AND CHILL

To determine the effect of section size, castings of 2½-in. dia. were made, having thicknesses of ½, 1 and 2 in. All were poured through the central riser. A ½-in. thick disk having a chill around the periphery was also cast from the same heat. This melt was heated and poured at the standard temperature of 2225°F.

As shown in Fig. 11, all the sand-cast specimens had low wear. The 1-in. section was equal to 80-10-10 and the other two were much superior, so that it should be possible to cast the alloy in various sizes and expect good wearing properties.

To check the indicated high wear rate of the chill casting, a second melt was made, part was cast into a chill mold and the rest into a sand mold of ½-in. section. These results confirmed the earlier work and show that the chilled material was

tion of comparatively coarse particles is desirable in nickel-antimony-lead bronze for best wear resistance.

CASTING CHARACTERISTICS

Shrinkage.—To develop additional information on the casting characteristics of the alloy, shrinkage cylinders were made and sectioned following the practice used by Pilling and Kihlgren¹¹ in their investigation of shrinkage. These cylinders, cast with the cylindrical axis horizontal, were 3¼-in. dia. by 3¼ in. long, and were gated through a horn gate. No risers were attached. A melt containing 10 per cent lead, 8 per cent nickel and 1 per cent antimony was made and allowed to cool until it started to solidify. It was then reheated and cylinders were poured 50° and 150°F. above the liquidus.

Both castings formed an external pipe in the cope. This characteristic is a desirable

one, as compared with the internal pipe, which is difficult to feed. The external pipe can be taken care of by adequate risers.

Effect of Sand.—Sound castings could be readily produced in ordinary green sand; however, in the production of bushing stock, it is customary to use a core. It is here that some difficulty was encountered. Cores that employed oil, cereal or resin binders invariably caused a thin layer of sub-skin porosity. This trouble was eliminated by the use of a cement-bonded core, which is a practical solution of the problem, for they are easily produced and require no baking. The mixture used contained 12 per cent Portland cement, 5 per cent water and balance silica sand. After molding, the core was allowed to stand 24 hr. in a moist atmosphere, to allow it to set and become hard. It was then placed in the green-sand mold.

CONCLUSIONS

Based upon microscopic examinations, compression tests and lubricated Amsler wear tests, the following conclusions are made:

1. A copper-base alloy containing 8 per cent nickel, 10 per cent lead, 2 per cent tin and 1 per cent antimony would appear to be a promising substitute for the 80 per cent copper, 10 per cent tin, 10 per cent lead bearing bronze when used in the sand-cast condition. The nickel-antimony-bronze has superior wearing qualities, equivalent compressive yield and lower ductility.

2. In applications designed for lower bearing pressures, the tin can be omitted from the nickel-antimony bronze and an alloy is obtained that has very high wear resistance, but the yield point is about 30 per cent lower.

3. The wear resistance of the nickel-antimony-lead bronzes investigated was related to the microstructure. Highest properties were obtained with lead in a

random dispersion and the presence of an antimony-containing compound. Intergranular lead films caused high wear.

4. In producing the alloy, excessive



FIG. 12.—CHILL-CAST ALLOY, 10 PER CENT LEAD, 8 PER CENT NICKEL, 1 PER CENT ANTIMONY COPPER. $\times 300$.

Etched with ammonium peroxide.

melting temperatures should be avoided and castings should be made in green sand or cement-bonded core sand. Chill-cast sections of the alloy had less wear resistance than others.

ACKNOWLEDGMENTS

The author wishes to thank Mr. N. B. Pilling, Director of the Research Laboratory, for his helpful suggestions, and Dr. E. N. Skinner and Mr. W. R. Hempstead for their assistance in conducting the experimental work.

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DISCUSSION

(P. A. Beck presiding)

J. K. ANTHONY.*—In looking over the data on Table 2, and as the author himself comments, there is a terrific difference in the wear tests with a rather small change in antimony content. The fifth alloy listed in Table 2 gives a weight loss of 50 mg., whereas the seventh gives a weight loss of 372 mg. The only appreciable difference between these two alloys was in 0.44 per cent of antimony. I believe that this range of alloy composition should be studied in a more detailed manner and actual limits for the antimony content should be established.

F. R. HENSEL.†—Were microhardness measurements made of the different constituents in the structure and compared with the Brinell hardness of the sand-cast material?

J. T. EASH (author's reply).—No microhardness measurements were made.

F. R. HENSEL.—How did the hardness of the chill-cast and a sand-cast alloy compare?

J. T. EASH.—The hardness of the material in the two conditions was about the same. The sand-cast hardness was 50 Brinell and the chill-cast wear disk was 57 Brinell.

A. I. BLANK.‡—Were any special variations noted because of differences in temperature or differences in moisture content of the air throughout the tests? The amounts of wear in weight loss seem rather large and the question arises as to whether true wear or something of a galling or scoring action was obtained.

J. T. EASH.—All of the wear tests were conducted at room temperature. Temperature

measurements of the rotating disks were not made during the test for it was thought the cooling action of the kerosene lubricant would eliminate their necessity. Variations in the moisture content of the air probably had a negligible effect on these tests because of the kerosene lubricant that covered the specimens at all times.

No galling or scoring was encountered in these specimens and all tended to develop a glossy surface.

F. R. HENSEL.—What was the surface condition of the steel disk?

J. T. EASH.—The steel disk was given a fine-grind finish, using a Norton 38120-J wheel.

F. R. HENSEL.—Did you measure the quality of the surface finish?

J. T. EASH.—Surface finish measurements were not made, but all the steel disks were ground with the same abrasive wheel to make the tests comparative.

G. P. HALLIWELL.*—My discussion is mostly in the form of questions. The first one has a bearing also on the paper by Bever and Floe (p. 128).

What information can be given concerning the melting conditions? What is meant by the term "castability"? It has been mentioned in specifications without any clear definition. Is there any explanation as to why superheating gives the lead structure mentioned? Is it the effect of superheating, per se, or the effect of the change in the cooling rate as a result of a greater quantity of heat in the surrounding mold material?

I would like to add a word of warning concerning the use of these test results based on kerosene as a lubricant. Because an alloy may show good results with kerosene does not necessarily mean it will behave likewise under an oil lubricant. I think we must be a little hesitant about translating a set of results to other conditions of higher pressure and speeds with oil as a lubricant.

The lead particle size and its distribution, especially if the metal shows marked columnar crystallization, may modify the mechanical

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† Consulting Engineer, P. R. Mallory & Co., Indianapolis, Indiana.

‡ Chase Brass and Copper Co., Waterbury, Connecticut.

* Director of Research, H. Kramer and Co., Chicago, Illinois.

properties materially. Has the author noted any difference in wear as influenced by such conditions?

J. T. EASH.—The alloys were melted in an induction furnace in an unlined clay graphite crucible. Complete details of operations are given on page 173.

In describing the "castability" of an alloy, one must consider a number of factors. To be considered good in this respect, the metal should pour clear from the crucible without the formation of detrimental films on the metal stream. It needs sufficient fluidity to fill the mold and should solidify quietly without the formation of laps or folds and internal shrinkage. The bearing alloys described are good in these respects and form an external pipe on solidifying.

The distribution of the lead has an important influence on the wear characteristics. Chunky particles produce good results, whereas the occurrence of intergranular films such as are caused by superheating should be avoided. The detrimental effect of superheating is not due to a change in the cooling rate of the casting as a result of a greater quantity of heat in the surrounding mold material; because the superheated metal that was cooled to the normal melting temperature, 2225°F., before pouring, had poor wearing characteristics. The formation of the narrow intergranular lead films as compared with the chunky lead particles is probably related to the temperature of the separation of liquid lead from the melt during the solidification cycle. Veszelka¹² shows that in leaded bronzes, liquid lead separates from the melt over a range of temperature before the copper-tin part of the alloy is completely solidified. A decrease in this temperature range of lead separation to cause the liquation to occur at the time of final solidification would produce the intergranular effects noted.

G. EDMUNDS.*—I should like to ask what effect these bearings have on the journals. There are several constituents in the micro-

structure that are not present in the straight⁸ 80-10-10.

P. A. BECK.*—Dr. Eash investigated the effect of alloy composition and of chill on the structure and on the wear resistance of leaded bronze sand castings. One of his conclusions, based on the Amsler wear test, was that intergranular lead films caused high wear and are detrimental.

The majority of the copper-lead automotive bearings are made by continuously casting the alloy on one side of a horizontal steel strip and by cooling extremely fast as compared with a sand casting.

Copper-lead aircraft bearings are made by casting into individual steel shells, but here too the solidification is very rapid in comparison with sand castings. The lead distribution is interdendritic. This is also true for the strip-cast bearings. In such bearings the interdendritic lead distribution is not considered detrimental. In fact, it is the one most commonly desired.

In the manufacture of bearings for automotive and aircraft-engine use, the Amsler wear test is not used at all, as far as I know, because the conditions obtaining in the Amsler wear test do not resemble the conditions of a bearing in a gasoline or diesel engine.

J. T. EASH.—The comments by Mr. Beck on the chill casting and structure of high-lead-copper aircraft-bearing alloys are of interest. These alloys contain a considerably greater quantity of lead than the nickel-antimony bronzes and probably behave differently under a given set of conditions. We have found from our Amsler tests that various alloys respond differently; i.e., some are impaired by chill casting while others are equally as good chilled or sand cast. So what may be considered good or bad for one alloy may not apply to another.

A distinction should be made between normal interdendritic lead and intergranular films as used in this paper. Usually lead occurs in an interdendritic pattern, since it is the last constituent to freeze in the bronze. When it is arranged in chunky particles, it has the desired form. However, if it separates

¹² J. Veszelka: *Mitt. Berg-Hutt. Abt., Hockschule Berg und Forstiv, Sapro (1932)* 4, 162.

* American Brake Shoe Co., Mahwah, New Jersey.

* Cleveland Graphite Bronze Co., Cleveland, Ohio.

• in thin films around the dendrites, particularly around the dendrite family grains, it has a large surface area and has a weakening effect out of proportion to the quantity present. This condition caused high wear.

It is believed that the nickel-antimony-lead bronzes will not have an injurious effect on

the usual journal materials. In the Amsler wear test, the steel showed practically no wear. Some of the tin-free material has given satisfactory service in commercial applications using sand-cast bushing bearings in such places as paper mills, winches, hoists and motor boats.

Physical Properties of Copper-manganese-zinc Alloys Containing 60 Per Cent Copper and 5 to 25 Per Cent Manganese

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(Chicago Meeting, February 1946)

THE comprehensive study of the copper-manganese-zinc alloy system in the Bureau of Mines Laboratories has so far been principally concerned with alloys that lie within the alpha solid solution field of the system. Two regions, one centering about 65 per cent copper, 10 manganese and 25 zinc, and the other centering about 70 per cent copper, 20 manganese, 10 zinc, have been carefully examined.^{1,2} These have indicated that when the alloys are made with electrolytic manganese considerable amounts may be readily introduced and that the strength and hardness are increased without excessive losses in ductility. In the course of the work of establishing the limits of the alpha solid solution range,³ enough of certain of the alloys was prepared to permit determination of their physical properties at a future date. The 60 per cent copper alloys concerned here are part of that series. They cross through the alpha field and into the adjacent alpha plus beta and alpha plus \bar{X} fields, and are of interest because they offer some information on the effects of manganese on alloys lying in these fields.

Manuscript received at the office of the Institute July 26, 1945. Issued as T.P. 1956 in METALS TECHNOLOGY, January 1946.

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¹ References are at the end of the paper.

COMPOSITION AND FABRICATION OF ALLOYS

The chemical composition of the alloys involved is given in Table 1. They were intended to contain 60 per cent copper with manganese increasing from 5 to 25 per cent in 5 per cent steps and zinc decreasing

TABLE 1.—*Chemical Composition of Alloys Studied*
PER CENT

Alloy No.	Cop- per	Manga- nese	Zinc	Al	Fe	Si
17	60.1	5	35.1	0.04	0.008	Nil
18	60.5	9.8	29.8	0.02	0.005	Nil
19	60.5	14.6	25.0	0.02	0.005	Nil
20	60.2	19.5	20.5	0.02	0.005	Nil
21	59.7	24.8	15.0	0.02	0.005	Nil
H936	60.6	28.8	10.7			
D934	59.3	35.1	5.4	0.05	0.02	Nil

from 35 to 15 per cent. The analyses are so close to the intended composition that the alloys will be referred to hereafter by their nominal compositions. They were finished into sheet by cold-rolling and intermediate annealing procedures calculated to produce sheet $\frac{1}{16}$ in. thick, cold-reduced by 20, 40, 60, and 80 per cent in thickness. Physical properties were determined on standard flat tensile specimens with 4-in. gauge length, although the test gauge section used was 2 in. The properties were obtained on cold-worked material and on material annealed at temperatures ranging from 700° to 1500°F. after 60 per cent cold reduction. Since an annealing temperature of 1200°F.

was used for all intermediate annealing in fabrication of the sheet, the material representative of the zero per cent cold-

obtained by quenching specimens of the alloys containing 5, 10, 15, 20, 25, 28.8, and 35 per cent manganese after 30 min.

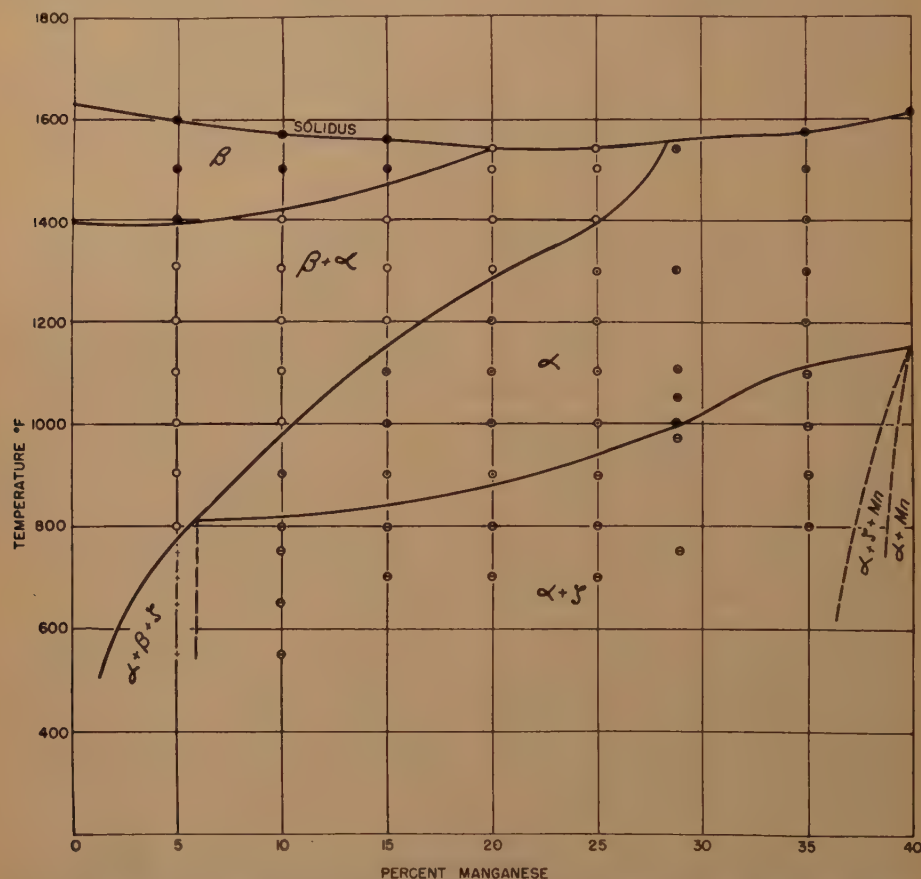


FIG. 1.—SECTION THROUGH COPPER-MANGANESE-ZINC TERNARY SYSTEM AT 60 PER CENT COPPER.

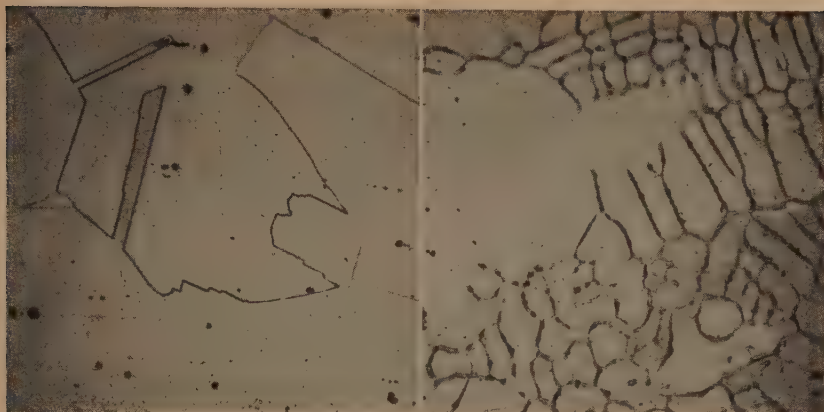
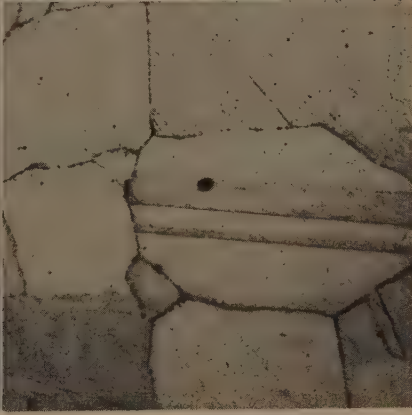
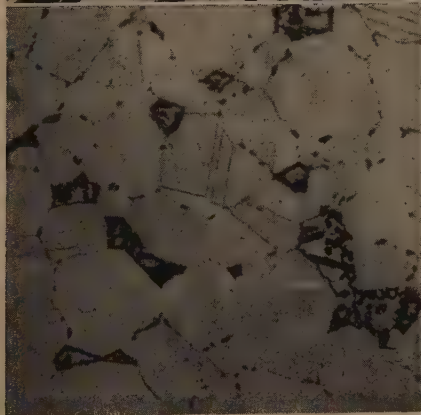
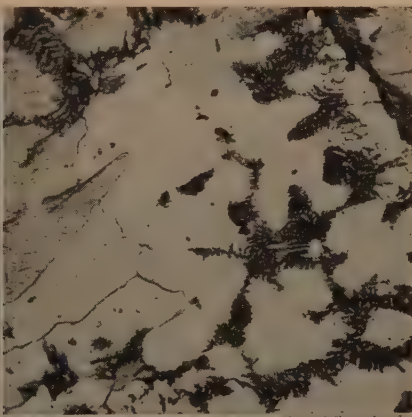
work state was also annealed at this temperature.

THE QUASI-BINARY SYSTEM AT 60 PER CENT COPPER

The quasi-binary system for alloys with a constant copper content of 60 per cent and with manganese varying from 0 to 40 per cent is given in Fig. 1. This diagram is drawn chiefly from metallographic data previously reported by these laboratories.³ Placing of the solidus required some additional data which were

at successively higher temperatures and examining for evidence of melting. The highest temperature to which they could be heated without microscopic signs of melting was taken as the solidus. In most cases visual evidence of melting agreed with microscopic examination.

Experience with the sluggish copper-manganese alloys⁴ has shown this approach, if carefully carried out, to be more reliable than the conventional thermal analysis. All specimens were heated in a purified helium atmosphere, and although some

FIG. 2.—35 PER CENT MANGANESE ALLOY QUENCHED FROM 1560°F. $\times 250$.FIG. 3.—35 PER CENT MANGANESE ALLOY QUENCHED FROM 1570°F. $\times 250$.FIG. 4.—15 PER CENT MANGANESE ALLOY QUENCHED FROM 1550°F. $\times 250$.FIG. 5.—15 PER CENT MANGANESE ALLOY QUENCHED FROM 1560°F. $\times 250$.FIG. 6.—5 PER CENT MANGANESE ALLOY AFTER 48 HOURS AT 550°F. $\times 500$.FIG. 7.—10 PER CENT MANGANESE ALLOY AFTER 48 HOURS AT 550°F. $\times 500$.

difficulty was encountered with certain compositions the results were quite satisfactory and sufficiently accurate for the purpose. The instability of the beta phase

Figs. 2 and 3 are characteristic of the alpha solid solution alloys after 30 min. just above and below the solidus. The change from the typically twinned struc-

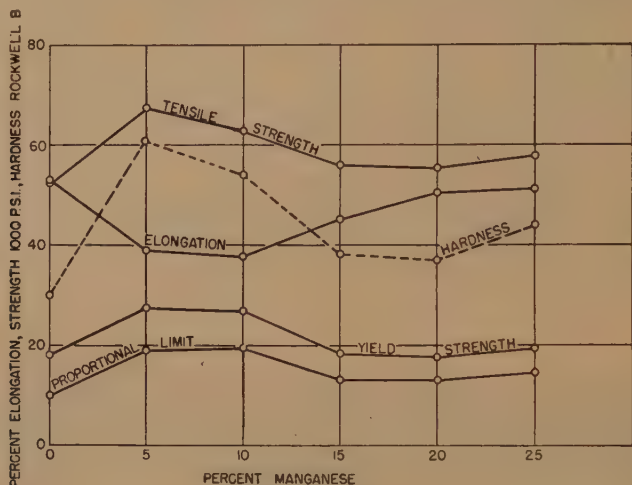


FIG. 8.—PROPERTIES OF ALLOYS CONTAINING 60 PER CENT COPPER, 0 TO 25 PER CENT MANGANESE, BALANCE ZINC, ANNEALED AT 1200°F.

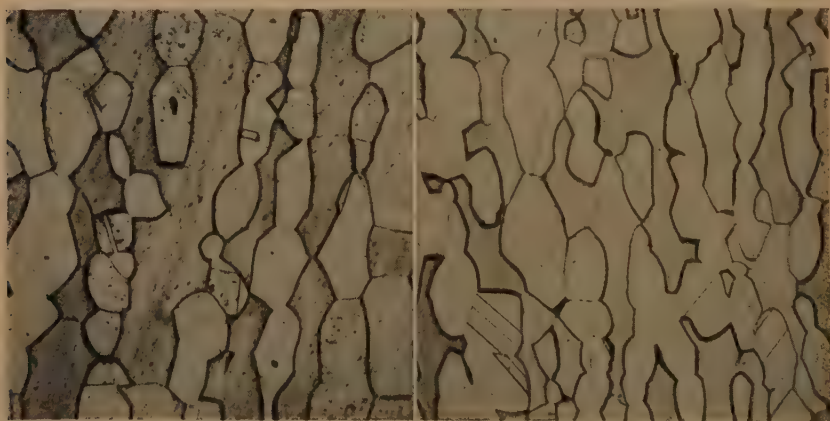


FIG. 9.—60-40 BRASS ANNEALED ONE HOUR AT 1200°F. WATER QUENCHED. $\times 250$.

FIG. 10.—5 PER CENT MANGANESE ALLOY ANNEALED ONE HOUR AT 1200°F. WATER QUENCHED. $\times 250$.

leading to the formation of alpha needles or massive transformation to alpha and the structures resulting from the peritectic reaction interfered with the typical signs of melting in some of the alloys, and for these visual indications of melting were taken as the criteria.

ture to a dendritic type illustrates very clearly the crossing of the solidus line and places the beginning of melting between 1560° and 1570°F. The structures shown in Figs. 4 and 5 are those of the 15 per cent manganese alloy at temperatures above and below the solidus for that

composition. The dendrites of Fig. 5 are not as well developed as those of Fig. 3 but definitely indicate melting at 1560° although not at 1550°F . Some of the other specimens gave visual signs of melting at temperatures below those producing definite microscopic indication and for these specimens the lower temperature was taken as the solidus.

The solidus points for zero manganese and for zero zinc are taken from published data on the copper-zinc and copper-manganese systems.^{5,4} Since no attempts were made to determine the liquidus or the peritectic points, these are not included in this diagram. The spread of the alpha-beta field at the solidus is, however, somewhat less than that suggested by Heusler, and while the data on the solidus determined by Heusler⁶ and by Bauer and Hansen⁷ do not cover this region to permit direct comparison, they are in general agreement with the trends indicated.

The X constituent indicated in the previous report on the alpha field has been found to have a face-centered cubic lattice with a parameter varying from about 6.90 to 6.99 Å. The present data are not sufficiently complete to define this phase more precisely at this time, but its varying parameter and its appearance under the microscope indicate that it is a three-component secondary solid solution, which occurs near the center of the diagram. Its occurrence, particularly in association with alpha and beta in the 5 per cent alloy, indicates that it corresponds to Bauer and Hansen's zeta and Heusler's epsilon in that region. It is designated in Fig. 1 as zeta rather than X and will be so referred to in this report.

The positions of alpha plus alpha-manganese, alpha plus alpha-manganese plus zeta, and alpha plus beta plus zeta fields are indicated by dotted lines. The first two are relatively narrow areas, which have not been definitely positioned, and only the third area, alpha plus beta plus

zeta, is significant for present study. The 5 per cent alloy is the only one to enter this field and does so only below 700°F . The microstructure of this alloy after 48 hr. at 550°F . following a "solution" treatment of 24 hr. at 800°F . is shown in Fig. 6; the zeta phase occurs in the grain boundaries of the alpha phase and dispersed throughout the beta phase. A similar treatment of the 10 per cent manganese alloy, as shown in Fig. 7, did not develop the beta phase but produced only the alpha solution with the zeta constituent as an intergranular precipitate. The boundary for this field is therefore indicated between 5 and 10 per cent manganese.

PHYSICAL PROPERTIES OF ANNEALED MATERIAL

The tensile properties of the alloys after cold-working, annealing at 1200°F . for 1 hr., and water quenching, are plotted in Fig. 8 as a function of manganese content. The proportional limits given in this chart correspond to the stress required to produce a 0.01 per cent offset from the modulus line and the yield strength corresponds to that for a 0.2 per cent offset. The properties for zero per cent manganese (60-40 brass) were taken from the charts of Wilkins and Bunn.⁸ They apply to 0.040-in. strip with a grain size of 0.045 mm. after annealing at 1200°F .

The decrease of properties with increasing manganese content above 5 per cent is at first glance surprising, but can be readily understood from a consideration of the pseudo-binary system in Fig. 1. At 1200°F . the 5, 10, and 15 per cent alloys are in the alpha plus beta field. This is evident from the microstructure of Figs. 9 to 14, which also permit an estimate of the relative amounts of the phases present. These structures show a slight decrease in the amount of beta with the first 5 per cent of manganese, a greater decrease with 10 per cent manganese, and

only a trace with 15 per cent manganese. At 20 and 25 per cent manganese the alloys are single phase (alpha solid solution).

The maximum strength of 66,500 lb. per sq. in. with 39 per cent elongation

phase and to some extent by the increasing grain size of the alpha groundmass. The minimum tensile strength of 55,000 lb. per sq. in. with 17,000 lb. per sq. in. yield strength and 50 per cent elongation occurs

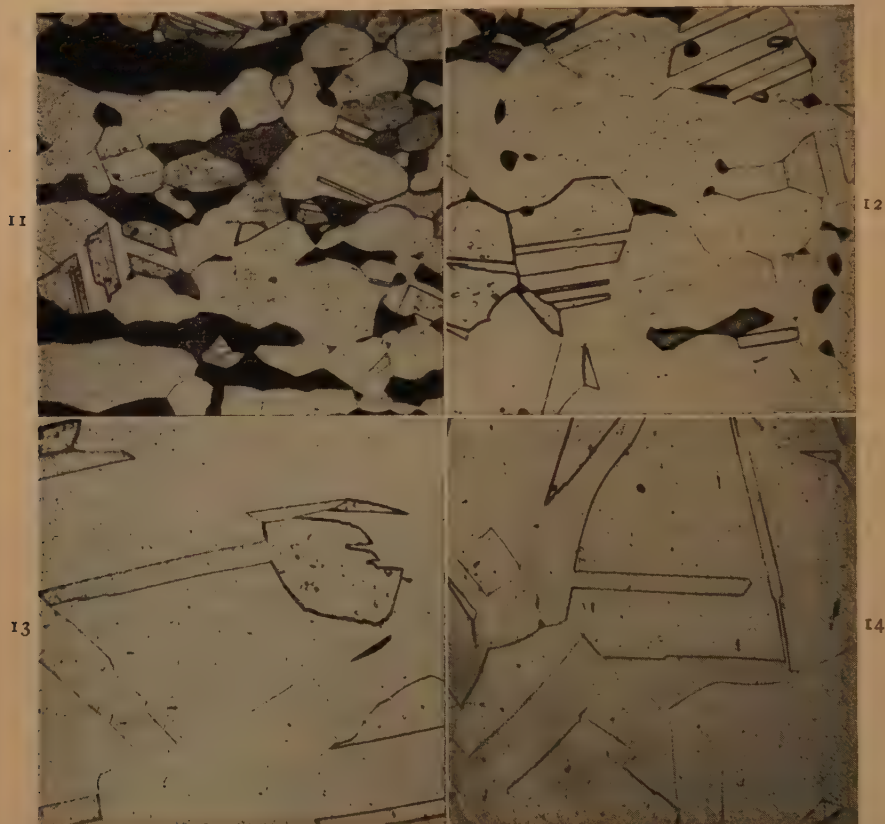


FIG. 11.—10 PER CENT MANGANESE ALLOY ANNEALED ONE HOUR AT 1200°F. WATER QUENCHED.
X 250.

FIG. 12.—15 PER CENT MANGANESE ALLOY ANNEALED ONE HOUR AT 1200°F. WATER QUENCHED.
X 250.

FIG. 13.—20 PER CENT MANGANESE ALLOY ANNEALED ONE HOUR AT 1200°F. WATER QUENCHED.
X 250.

FIG. 14.—25 PER CENT MANGANESE ALLOY ANNEALED ONE HOUR AT 1200°F. WATER QUENCHED.
X 250.

occurs in the 5 per cent manganese alloy. As this alloy has about the same amount of beta as the 60-40 brass, its higher strength must be due chiefly to the manganese in the alpha phase, since this is the continuous phase. The decreasing strength with higher manganese is caused by the decrease in the amount of the beta

in the 20 per cent manganese alloy, which is single-phase alpha under these conditions. Typical published properties for a 65-35 brass, about the highest zinc content brass that will be single phase under these conditions, are 42,000 lb. per sq. in. tensile strength, 10,000 lb. per sq. in. yield strength, and 70 per cent

elongation in 2 in. for material annealed at 1200°F. and having a grain size equivalent to that of the manganese alloy. These properties are well below those of the manganese alloy and indicate the strengthening effect of manganese on the alpha solid solution. The addition of more manganese produces slightly greater strength without decreasing the elongation, as shown by the properties of the 25 per cent manganese alloy.

increased as the amounts of beta phase decreased.

EFFECT OF COLD-WORKING

Physical properties of the alloys in the various stages of cold-work are given in Table 2. Data for the 5 per cent and 25 per cent manganese alloys are also plotted in Figs. 15 and 16 as a function of reduction in thickness by cold-rolling. As might be expected from Fig. 8, the 5 per cent alloy

TABLE 2.—*Variation in Physical Properties with Cold-rolling*

Percentage of Mn in Alloy	Cold Reduction Per Cent	Ultimate Strength Lb. per Sq. In.	Yield Strength, Lb. per Sq. In. 0.2 Offset	Proportional Limit, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Hardness, Rockwell B
5	0	67,200	27,200	19,000	39	61
	20	82,000	73,000	55,000	16	90
	40	98,000	84,500	60,500	6	96
	60	105,000	93,500	62,000	4.6	98
	80	115,000	103,000	75,000	3.0	102
10	0	62,600	26,600	16,900	37.8	54
	20	78,500	70,500	54,000	10.1	88
	40	95,000	86,500	66,500	4.6	96
	60	106,000	97,000	69,000	2.7	100
	80	116,000	106,000	72,000	2.2	102
15	0	56,000	18,100	13,400	45	38
	20	74,400	66,600	54,000	14.3	85
	40	92,000	85,600	65,000	5	94
	60	100,700	96,100	69,100	3.4	98
	80	110,000	104,000	75,000	3.0	100
20	0	55,500	17,700	13,000	50.5	37
	20	68,500	57,000	43,000	19.5	82
	40	86,200	82,100	63,500	4.6	92
	60	97,600	91,500	67,000	3.6	96
	80	108,000	101,500	70,000	3.4	100
25	0	57,900	19,300	14,500	51	44
	20	72,000	61,500	44,000	14	84
	40	92,600	88,000	71,500	4.3	94
	60	102,500	97,900	69,500	3.1	97
	80	109,500	103,000	73,000	2.9	100

The hardness curve follows the same general trend as the tensile strength, showing a maximum at 5 per cent manganese and a minimum at 20 per cent. The steeper gradients of the hardness curve suggest that in the ranges concerned hardness is more sensitive than tensile strength to changes in composition.

The effect of manganese on grain size cannot be evaluated from these data because of the presence of the beta phase in the first three alloys, but it should be noted that the size of the alpha grains

exhibits the highest strength and hardness in all stages of the working. All five of the alloys, however, show about the same rate of work-hardening and approach strengths of 105,000 to 115,000 lb. per sq. in. with 80 per cent cold-work. The 20 and 25 per cent manganese alloys have, of course, the highest elongation in the zero cold-worked state and still have 20 per cent elongation after 20 per cent cold-rolling, while the 5, 10, and 15 per cent manganese alloys range between 10 and 16 per cent elongation after 20 per cent cold-work.

There is, however, very little difference in elongation between any of the alloys beyond 40 per cent reduction. In the alloys composed of a mixture of alpha and beta solid solutions, the proportional limit and yield strengths increase rapidly with the first 20 per cent cold-work and then more slowly with additional working. In the 20 and 25 per cent alloys, however, the proportional limit and yield strengths increase rapidly and at about the same rate up to 40 per cent cold-work and then increase more slowly. The significance of this difference between the working of the alpha solid solution and the mixture of the alpha and beta solid solutions is not clear. It is noteworthy that the 5 per cent manganese alloy can be cold-worked to 80 per cent reduction in thickness notwithstanding the presence of about 50 per cent beta solid solution. This indicates that manganese has not embrittled the beta phase and does not impair its working qualities. In all of the alloys the hardness curves show the same pattern, a rapid increase for the first 20 per cent cold-working and then a slower increase for additional cold-working. A maximum hardness of 102 Rockwell B is obtained with 80 per cent cold-work in the 5 and 10 per cent manganese alloys. The other three reach Rockwell B-100 with this same amount of cold-working.

EFFECT OF ANNEALING TEMPERATURE ON PROPERTIES OF COLD-WORKED ALLOYS

The properties obtained on material annealed at temperatures ranging from 400° to 1500°F. after 60 per cent reduction in thickness by cold-rolling are given in Table 3. Data for the 5 per cent and 25 per cent manganese alloys are also plotted as a function of annealing temperature in Figs. 15 and 16. The specimens for this work were held at temperature for one hour and water quenched. The curves for the 5 per cent alloy are representative

of the changes that occur in the range of 5 to 15 per cent manganese and show decreasing strength and hardness and increasing elongation as the annealing temperature increases to 1000° or 1100°F. These changes correspond to normal relief of strain and recrystallization followed by grain growth and are further conditioned by the increasing amount of the alpha solid solution, which reaches a maximum in about this temperature range. The temperature at which maximum elongation occurs corresponds to that for minimum strength and hardness. Beyond this temperature the hardness and strength increase and the elongation decreases, owing to the formation of increasing amounts of the beta phase. This is best shown by the 5 per cent manganese alloy where the trend is maintained up through 1400°F. This alloy annealed at 1500°F. should show similar results, but the tensile strength drops off markedly because of the decomposition of the beta phase on quenching from the annealing temperature. The beta solid solution of this composition is not stable and cannot be retained by quenching. The properties, therefore, are intermediate between those corresponding to beta and alpha. The decomposition of the beta solution also affects the properties of the 10 and 15 per cent manganese alloys annealed at temperatures beyond 1300°F. From 1100° to 1300°F. the hardness and strength are increasing but they drop off after higher temperature treatment, owing to the transformation of the beta during the cooling. This transformation is not directly reflected by the elongation curves, because of the transformation of considerable beta to the needlelike formation of the alpha phase. Representative microstructure of the 15 per cent alloy quenched from 1400° and 1500°F. are given in Figs. 17 and 18. They illustrate the decomposition of the beta solid solution and the formation of the alpha needles characteristic of these

TABLE 3.—*Variation in Physical Properties with Annealing Temperature*

Annealing Temperature, Deg. F.	5 Per Cent Manganese					10 Per Cent Manganese					15 Per Cent Manganese					20 Per Cent Manganese					25 Per Cent Manganese				
	Ultimate Tensile Strength, Thousands Lb. per Sq. In.	Yield Strength, 0.2 Offset, Thousands Lb. per Sq. In.	Proportional Limit, Thou- sands Lb. per Sq. In.	Elongation, Per Cent	Hardness, Rockwell B	Ultimate Tensile Strength, Thousands Lb. per Sq. In.	Yield Strength, 0.2 Offset, Thousands Lb. per Sq. In.	Proportional Limit, Thou- sands Lb. per Sq. In.	Elongation, Per Cent	Hardness, Rockwell B	Ultimate Tensile Strength, Thousands Lb. per Sq. In.	Yield Strength, 0.2 Offset, Thousands Lb. per Sq. In.	Proportional Limit, Thou- sands Lb. per Sq. In.	Elongation, Per Cent	Hardness, Rockwell B	Ultimate Tensile Strength, Thousands Lb. per Sq. In.	Yield Strength, 0.2 Offset, Thousands Lb. per Sq. In.	Proportional Limit, Thou- sands Lb. per Sq. In.	Elongation, Per Cent	Hardness, Rockwell B	Ultimate Tensile Strength, Thousands Lb. per Sq. In.	Yield Strength, 0.2 Offset, Thousands Lb. per Sq. In.	Proportional Limit, Thou- sands Lb. per Sq. In.	Elongation, Per Cent	Hardness, Rockwell B
As rolled	105.5	63.5	62.0	4.6	86	106.0	67.0	66.0	2.7	100	100.7	96.1	69.1	3.4	86	97.6	61.5	67.0	3.6	96	102.5	97.9	69.4	3.1	97
400	96.5	80.0	62.5	9.0	98	99.0	90.0	66.5	4.6	98	100.0	92.5	71.5	4.6	98	96.5	92.1	73.0	3.5	97	97.8	93.5	70.6	3.7	98
500	93.0	76.0	60.0	12.2	96	102.6	88.5	66.0	4.7	97	99.6	88.0	67.2	5.4	96	93.0	84.5	66.7	5.9	95	96.2	87.0	66.9	5.4	95
600	89.0	70.0	46.5	15.0	94	98.0	82.6	57.0	4.1	97	90.0	78.1	46.4	6.6	93	86.1	75.8	54.6	8.6	92	90.0	79.2	60.4	9.7	93
700	72.0	44.5	34.5	26.0	77	73.1	45.5	33.8	19.0	84	77.0	53.0	41.5	16.5	84	81.7	67.3	51.5	13.0	89	84.5	69.0	54.6	13.2	90
800	66.5	33.0	29.0	35.0	63	66.1	37.2	31.4	29.5	68	67.3	33.4	33.0	33.2	64	67.6	29.4	24.9	35.5	62	73.4	37.2	29.3	29.0	73
900	63.5	28.0	25.0	40.0	57	61.6	26.2	22.4	42.0	53	61.6	25.9	23.3	40.0	55	63.1	25.5	21.3	39.0	55	67.5	28.5	24.8	34.1	62
1000	62.1	25.2	20.0	36.5	52	58.4	23.0	19.5	36.1	50	57.3	20.6	16.7	43.8	45	59.8	20.9	15.9	44.0	48	63.2	23.6	19.2	43.0	55
1100	63.0	23.1	17.1	42.0	52	58.7	22.0	13.3	40.4	50	55.2	18.3	13.2	48.1	40	56.8	18.7	12.6	48.1	44	60.8	21.1	17.7	46.5	50
1200	67.2	27.2	19.0	39.0	61	62.7	26.6	19.9	37.8	54	56.0	18.1	13.4	45.0	38	55.5	17.7	13.0	50.5	37	57.9	19.3	14.5	51.0	44
1300	73.1	33.5	21.0	31.0	67	67.5	29.5	18.9	32.0	62	66.8	23.6	13.0	35.0	58	53.8	18.0	13.0	47.0	40	54.4	18.6	13.2	49.0	39
1400	75.0	43.0	22.0	24.2	73	67.0	30.0	21.0	29.6	62	64.5	25.0	14.5	32.0	58	60.3	21.9	14.5	37.0	52	52.5	18.3	12.7	50.5	39
1500	67.0	39.0	21.5	12.5	79	66.0	33.2	20.0	26.5	77	59.0	25.2	17.0	29.0	54	57.0	23.9	13.3	31.7	48	57.3	22.2	15.2	41.5	50

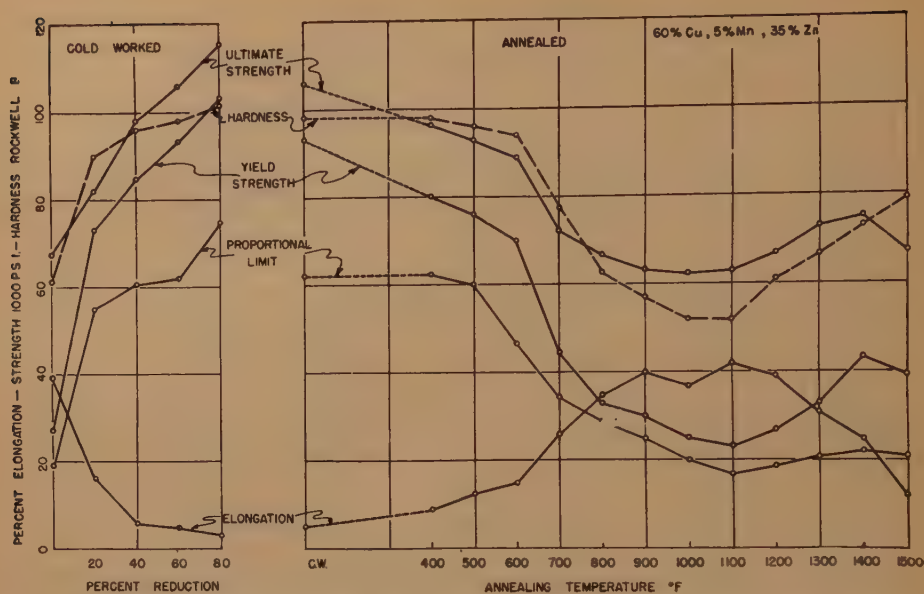


FIG. 15.—EFFECT OF COLD-WORKING AND SUBSEQUENT ANNEALING ON PROPERTIES OF ALLOY CONTAINING 60 PER CENT COPPER, 5 PER CENT MANGANESE, 35 PER CENT ZINC.

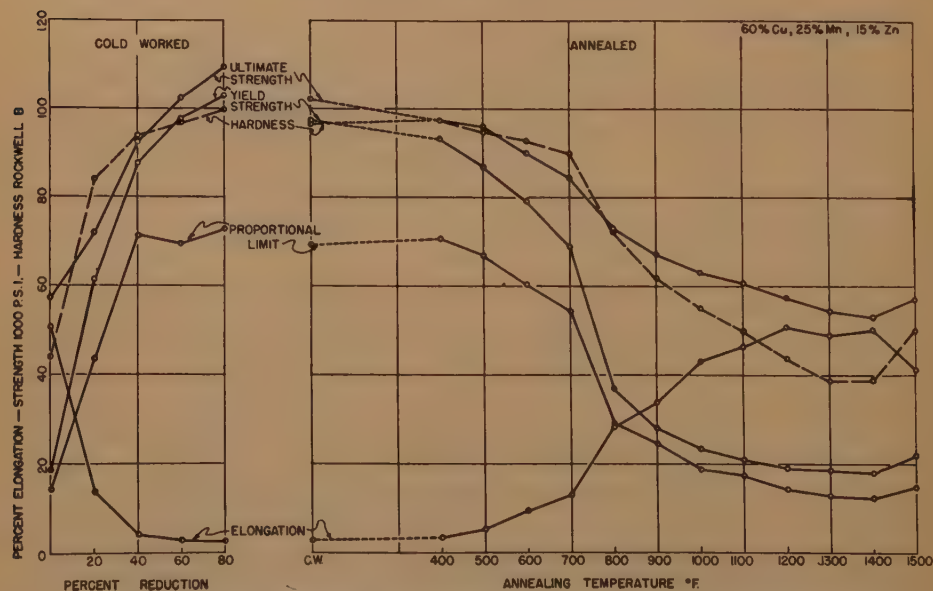
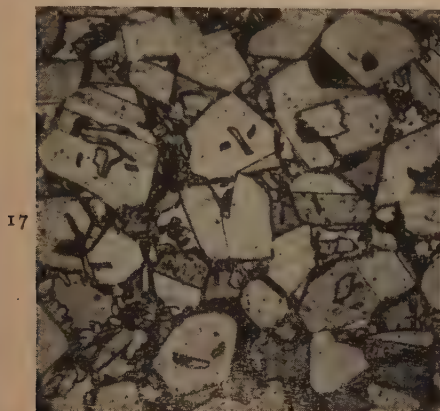


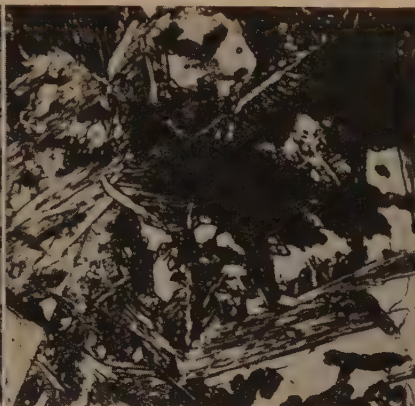
FIG. 16.—EFFECT OF COLD-WORKING AND SUBSEQUENT ANNEALING ON PROPERTIES OF ALLOY CONTAINING 60 PER CENT COPPER, 25 PER CENT MANGANESE, 15 PER CENT ZINC.

alloys. It is obvious from these data that annealing to obtain dead-soft material with a maximum elongation should be conducted in the range of 900° to 1000°F.

size of the alpha solid solution and by the introduction of the beta phase at still higher temperatures. At 1500°F. a considerable portion of beta is formed in both



17



18

FIG. 17.—15 PER CENT MANGANESE ALLOY ANNEALED ONE HOUR AT 1400°F. WATER QUENCHED. $\times 250$.

FIG. 18.—15 PER CENT MANGANESE ALLOY ANNEALED ONE HOUR AT 1500°F. WATER QUENCHED. $\times 250$.

for the 10 per cent alloy and 1000° to 1100°F. for the others. Recrystallization in the 5 per cent alloy occurs between 600° and 700°F., increasing to 700° to 800°F. in the 15 per cent alloy.

The 10 per cent alloy differs from the 5 and 15 per cent alloys in that it shows an increase in strength and hardness after treatment at 500°F. Although the increases are small, they suggest that the zeta phase may be capable of producing an age-hardening effect in some copper-manganese-zinc alloys.

The properties of the 25 per cent manganese alloys are plotted in Fig. 16 and are also representative of the 20 per cent alloy. These curves follow the same general trends noted above, with the tensile strength reaching a minimum of 52,500 lb. per sq. in. at 1400°F. Recrystallization in this alloy takes place at about 800°F. The strength and hardness are not greatly affected by the presence of the zeta phase at temperatures below 900°F. They appear to be more affected by an increase in grain

of these alloys, and, as in the others, it cannot be retained by rapid cooling and is decomposed into alpha solid solution needles. Minimum hardness and strength, combined with maximum ductility, occur on annealing at 1300° to 1400°F.

SUMMARY

Copper-manganese-zinc alloys containing 60 per cent copper and 5 to 25 per cent manganese as annealed at 1200°F. vary in tensile strength from 67,000 to 55,000 lb. per sq. in. The maximum strength occurs in the 5 per cent manganese alloy, which has a tensile strength of 67,000 lb. per sq. in. and a yield strength of 27,500 lb. per sq. in., Rockwell hardness of B-61 and an elongation of 39 per cent. The alloy is two-phase when annealed at this temperature, consisting of about 50 per cent alpha and 50 per cent beta solid solution. Increasing the manganese content decreases the amount of the beta phase, decreasing the strength and hardness. At 20 per cent manganese the alloys become

single-phase alpha solid solution alloys with a tensile strength of 55,000 lb. per sq. in., a yield strength of 28,000 lb. per sq. in., a Rockwell hardness of B-37 and an elongation of 50 per cent. Further increase in manganese appears to increase the strength and hardness slightly without decreasing the elongation.

The alloys are amenable to cold-working, being readily worked by cold-rolling to at least 80 per cent reduction in thickness. The ability of the 5 per cent alloy to undergo this deformation in the presence of the large amount of the beta phase is noteworthy. Cold-working produces a tensile strength of 115,000 lb. per sq. in., a yield strength of 103,000 lb. per sq. in., a hardness of Rockwell B-102 and an elongation of 3 per cent in 2 in. in the 5 per cent manganese alloy, and a tensile strength of 108,000 lb. per sq. in., a yield strength of 102,000 lb. per sq. in., a hardness of Rockwell B-100, and an elongation of 3 per cent in the 20 per cent manganese alloy.

These alloys annealed at temperatures ranging from 400° to 1500°F. after 60 per cent cold-working show the usual changes associated with strain relief, recrystallization, and grain growth. Recrystallization after 60 per cent cold reduction takes place between 600° and 700°F. for the 5 and 10 per cent manganese alloys and between 700° and 800°F. for the alloys higher in manganese. The 5, 10, and 15 per cent manganese alloys reach minimum elongation upon annealing at temperatures of 1000° to 1100°F. This corresponds to the minimum amount of the beta solid solution in their microstructures. Higher

annealing temperatures produce an increase in tensile strength and hardness with a corresponding decrease in elongation because of increasing amounts of the beta constituent found at these temperatures. The beta solution is not stable under all the conditions used in this work. It transforms during the quenching, usually with the formation of a needlelike alpha-solution structure, although it may also transform into massive alpha grains. The instability of the beta makes it impossible to determine the physical properties of this phase in these alloys. When it constitutes 50 per cent or less of the structure of the alloy, beta appears to be fairly stable and has a significant effect on the properties. The 20 and 25 per cent alloys do not exhibit beta unless they are heated to temperatures above 1300° and 1400°F., respectively.

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Tensile Properties of Aluminum-alloy Sheet at Elevated Temperatures

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(New York Meeting, October 1945)

It is necessary occasionally to use aluminum-alloy sheet where moderately elevated temperatures are encountered. Considerable attention has been directed toward determining the influence of "artificial aging" on the room-temperature properties of the precipitation-hardenable alloys, as testified by numerous company reports and by references 1 to 4. Investigations on the properties at elevated temperatures are few, however,⁵⁻⁷ and have not always covered the range of times and temperatures of greatest interest. The present investigation was instituted to overcome this deficiency. The work was done for the Office of Production Research and Development of the War Production Board, under the supervision of the War Metallurgy Committee, as a part of the "restricted" Project NRC-548. It has been released for publication by the Office of Production Research and Development.

As is well known, the high-strength aluminum alloys achieve their remarkable properties as a result of precipitation-hardening. In production they are subjected to a solution heat-treatment followed by quenching, to retain the supersaturated solid solution. The solution treatment is followed by "aging" (precipitation-hard-

ening) either at room temperature or at a suitable elevated temperature. A considerable increase in tensile and compressive yield stresses results from precipitation at room temperature ("natural aging"). Through the elevated-temperature process ("artificial aging") it is possible to obtain values of yield stress considerably higher than those attainable by natural aging. The increase in yield stress is accompanied by a smaller gain in ultimate tensile stress and by a decrease in elongation. During

TABLE I.—Sources of Materials Used in the Testing Program

MATERIAL	ORIGIN AND TREATMENT
24S-T Alclad....	From Lockheed stock.
24S-RT Alclad...	Direct from mill.
24S-T80 Alclad...	24S-O Alclad from Lockheed stock, solution-heat-treated (925°F., water quench) and aged at 375°F. for 10 ± ½ hour.
24S-T81 Alclad..	24S-T Alclad from Lockheed stock, plant stretched up to 1 per cent and aged 10 ± ½ hr. at 375°F.
24S-T86 Alclad..	24S-RT Alclad from Lockheed stock aged 5½ ± ½ hr. at 375°F.
61S-W (bare)....	From Lockheed stock.
61S-T (bare)....	61S-W (bare) from Lockheed stock aged 8 hr. at 350°F.
XB75S-T Alclad.	From Lockheed stock.

the first stages of artificial aging the yield stress increases steadily until it reaches a maximum value. In this condition the material is said to be "fully aged." Further exposure results in "overaging," attended by a steady decrease in yield stress. In the production of the artificially aged materials, temperatures and times are selected to achieve full aging. The following important characteristics are associated with the process:

1. The higher the temperature, the more rapidly is the fully aged condition attained.

Manuscript received at the office of the Institute April 9, 1945. Issued as T.P. 1929 in METALS TECHNOLOGY, December 1945.

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§ References are at the end of the paper.

2. In the case of the alloy 24S, the yield stress attainable is influenced by the application of cold-work preceding the aging treatment. The greater the degree of deformation, the greater is the yield stress attainable.

For the purpose of this paper it is convenient to classify the high-strength materials as follows:

Group A. "Naturally aged" materials—precipitation-hardenable alloys that have been solution-heat-treated and aged at room temperature.

Group B. "Artificially aged" materials—precipitation-hardenable alloys that have been solution-heat-treated and aged at elevated temperatures.

This classification permits obvious generalizations on the response of each group to further elevated-temperature exposure.

SCOPE OF THE INVESTIGATION

The following materials were included in the investigation:

GROUP A

- 0.040-in. 24S-T Alclad sheet
- 0.064-in. 24S-RT Alclad sheet
- 0.040-in. 61S-W bare sheet

GROUP B

- 0.040-in. 24S-T80 Alclad sheet
- 0.040-in. 24S-T81 Alclad sheet
- 0.040-in. 24S-T86 Alclad sheet
- 0.040-in. 61S-T bare sheet
- 0.040-in. XB75S-T Alclad sheet*

Tensile tests were performed on each material to determine: (1) ultimate tensile stress, (2) tensile yield stress, (3) elongation in 2 in., (4) primary and secondary moduli of elasticity, (5) tangent moduli for all stresses up to the tensile yield stress. All tests were made with a crosshead speed of 0.06 in. per min. and with specimens stressed transverse to the direction of rolling. Temperatures investigated included

75°F., 212°F., 300°F., and 375°F. At each of the elevated temperatures exposure periods ranged from ¼ hr. to 1000 hours.

MATERIALS INVESTIGATED

With the exception of the 24S-RT sheet, materials were furnished by the Lockheed Aircraft Corporation at Burbank. The 24S-T, 61S-W and XB75S-T sheets were taken from stock in the condition furnished by the mill; the remaining sheets consisted of similar material heat-treated at Lockheed to obtain the desired conditions. The Lockheed treatments are listed in Table 1. The 24S-RT sheet was obtained directly from the mill, by the University of California. All specimens of each material were taken from a single sheet.

Original room-temperature tensile properties are listed in Table 2, where they are compared with the allowable values published in ANC-5 and with typical and minimum values cited by the Aluminum Company of America. The original properties may be considered typical except in 24S-T80, where modulus values are lower than anticipated.

The nominal chemical compositions of the alloys^{1,5} are as follows:

- 24S..... 4.5 per cent copper, 0.6 manganese, 1.5 magnesium; remainder aluminum and normal impurities.
- 61S..... 0.25 per cent copper, 0.6 silicon, 1.0 magnesium, 0.25 chromium; remainder aluminum and normal impurities.
- 75S..... No information has been released on the precise composition. The principal hardening elements are zinc and magnesium with smaller additions of copper and other elements.

Standard heat-treatments for the materials tested are:

- 24S-T..... 24S alloy solution-heat-treated at 910° to 930°F. followed by quenching in cold water and aging at room temperature.
- 24S-RT... 24S-T strain-hardened by rolling to a reduction of about 5.5 per cent.

* This material is now designated 75S-T by its producer, the Aluminum Company of America.

61S-W....	61S alloy solution-heat-treated at 960° to 980°F followed by quenching in cold water and aging at room temperature.
24S-T80...	24S-T aged 10 hr. at 375°F. or 13 hr. at 365°F. without previous stretching.
24S-T81...	24S-T stretched 1 per cent and aged 10 hr. at 375°F. or 12 hr. at 365°F.
24S-T86...	24S-RT aged 5½ hr. at 375°F. or 8½ hr. at 365°F.
61S-T....	61S-W aged 8 hr. at 350°F. or 18 hr. at 320°F.
XB75S-T..	75S alloy solution-heat-treated at 860° to 930°F. followed by quenching in cold water and aging 24 hr. at 250°F.

PREPARATION OF SPECIMENS

Machining of the specimens was carried out by the Lockheed Aircraft Corporation at Burbank. All specimens of each material were taken from a single sheet. Dimensions are shown in Fig. 1, which conforms to the A.S.T.M. Standard E8-42. The edges of the reduced section were polished by hand with grade 320 emery, after which the width and thickness of each specimen were

measured to the nearest 0.0002 in. All specimens were of 0.040 or 0.064 in. nominal thickness, with the axis transverse to the direction of rolling.

Previous to testing, specimens were maintained for the desired holding periods in carefully controlled oil-bath furnaces, after which they were stored until required for tensile testing. The storage period ranged from two days to two months.

Houghton tempering oil No. 80 was used in the oil baths at all temperatures except 375°F. The temperature variations in the central 6 in. of specimens in these baths were known to be no greater than $\pm 2^\circ\text{F}$. temporal and $\pm 1^\circ\text{F}$. spatial, except for brief drops attending the insertion of additional specimens. After removal of specimens from the baths, all oil was wiped off before storage. The 375°F. specimens were heated in an oil of unspecified composition, by the Lockheed Aircraft Corporation. Over-all temperature variations were known to be $\pm 2^\circ\text{F}$.

TABLE 2.—Room-temperature Tensile Properties of the Materials Compared with Published Minimum and Typical Values

Material	Tensile Yield Stress, 1000 Lb. per Sq. In. Alcoa			Ultimate Tensile Stress, 1000 Lb. per Sq. In., Alcoa			Elongation, Per Cent in 2 In.			Primary Modulus, 10 ⁶ Lb. per Sq. In.		Secondary Modulus, 10 ⁶ Lb. per Sq. In.	
	NRC-548 Material ^a	Specified Minimum ^b	Alcoa Typical ^c	NRC-548 Material ^a	Specified Minimum ^b	Alcoa Typical ^c	NRC-548 Material ^a	Specified Minimum ^b	Alcoa Typical ^c	NRC-548 Material ^a	ANC-5 Allowable ^d	NRC-548 Material ^a	ANC-5 Allowable ^d
24S-T													
Alclad...	43.3	39	43	64.8	59	64	17.0	12	18	10.4	10.5	9.2	9.5
24S-RT													
Alclad...	52.3	50	53	67.0	66	67	10.6	10	11	10.6	10.5	9.7	10.0
24S-T80													
Alclad...	51.6			65.0			10.0			9.9	10.5	9.0	9.5
24S-T81													
Alclad...	58.9	54	60	65.2	62	66	5.3	5	7	10.4	10.5	9.3	9.5
24S-T86													
Alclad...	66.6	62	66	70.4	66	70	4.5	3	6	10.3	10.5	9.1	9.5
61S-W													
(Bare)...	23.2	16	21	36.8	30	35	20.2	16	22	10.0			
61S-T													
(Bare)...	38.3	35	39	44.1	42	45	12.0	10	12	10.1	10.0		
XB75S-T													
Alclad...	67.0	62	66	78.0	72	76	10.3	8	11	9.9		8.8	

^a The NRC-548 specimens were stressed transverse to the direction of rolling. In the published values listed above, the direction of stress is generally not specified.

^b Aluminum Company of America, "Alcoa Aluminum and Its Alloys," 1944. Section on Mechanical Properties Specifications. These values are generally the same as the corresponding ANC-5 Allowables.

^c *Ibid.*, section on Typical Mechanical Properties.

^d Army-Navy-Civil Committee on Aircraft Design Criteria, "Strength of Aircraft Elements," ANC-5 Amendment 1, Oct. 22, 1943.

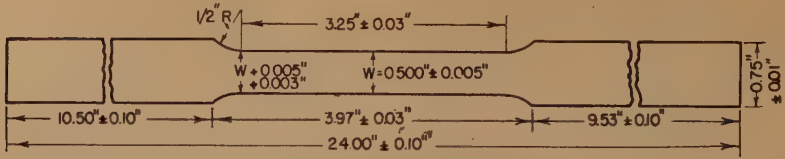


FIG. 1.—TENSILE SPECIMEN.

Sheet thickness $\begin{cases} 0.040 \text{ in. (nominal).} \\ 0.064 \text{ in.} \end{cases}$

Taper: gradual taper from ends of reduced section of middle.

Finish: edges inside gauge length to be finished with grade 320 emery, removing all milling marks.

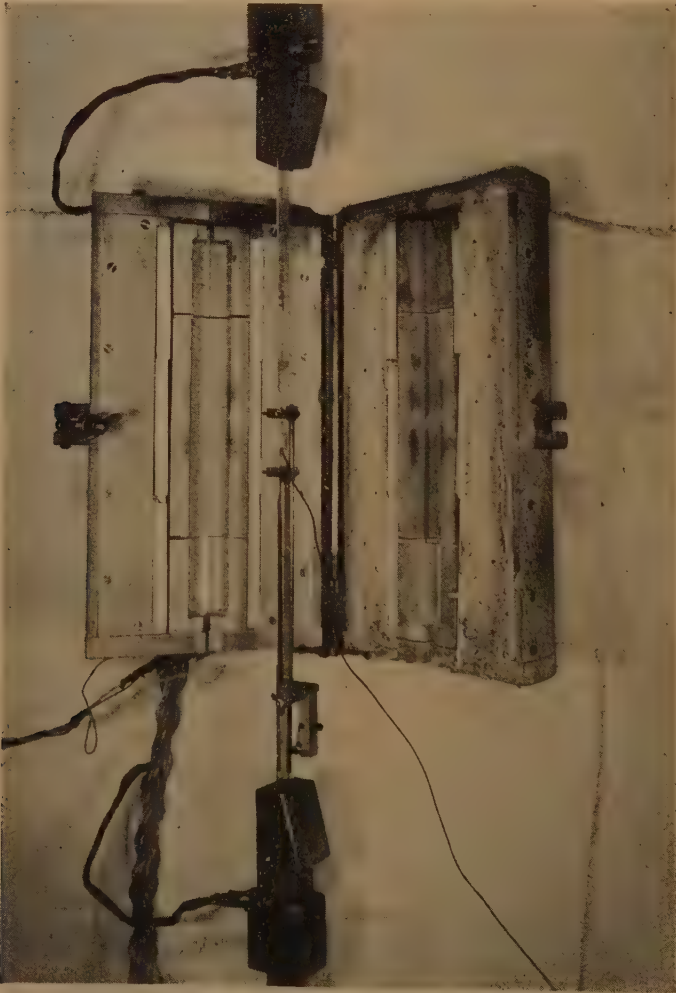


FIG. 2.—FURNACE AND AUXILIARY HEATING CONNECTIONS.

HEATING AND TEMPERATURE CONTROL

Following storage, specimens were tested in tension at the temperatures previously used in the oil baths. They were brought to temperature in the testing machine in approximately two minutes, after which they were maintained throughout the holding and testing periods with a temporal variation no greater than $\pm 3^{\circ}\text{F.}$ at all temperatures employed. Testing was started 15 min. after specimens were placed in the furnace.

Two separate sources of heat were employed in the testing machine. The first was a split cylindrical furnace 17 in. long and having three banks of heating elements arranged vertically, as shown in Fig. 2. The voltage across each bank was adjusted separately, thus aiding in control of the temperature gradient. To secure rapid heating of the specimen, an auxiliary source of heat was provided by passing a controlled current through the specimen itself. The auxiliary current, which was introduced through flexible copper leads attached to the grips, was gradually reduced as the specimen approached the desired furnace temperature. The controlling pyrometer governing the furnace was set for a temperature slightly lower than that desired in the specimen, so that near thermal equilibrium a small auxiliary current allowed precise control of the specimen temperature. When this current was reduced to zero, just prior to testing, the resultant drop in temperature was negligible.

Temperature measurement was obtained from a glass-sheathed 30-gauge iron-constantan thermocouple attached to the center of the gauge length of each specimen. The couple was secured to the surface by several turns of light, flexible spun-glass sheathing (Fig. 3). Such a couple does not indicate the true surface temperature of the specimen, since it is in contact with the glass wrapping. Through the use of

peened-in couples, however, it was established that at 300°F. the actual specimen temperature was from 0° to 3°F. lower than indicated by the surface thermo-



FIG. 3.—EXTENSOMETER ASSEMBLY AND THERMOCOUPLE ATTACHMENT.

couple. Suitable corrections were applied at all temperatures.

The temperature distribution along specimens was also investigated by means of peened-in couples. At 300°F. the overall spatial variation was found to be $\pm 2^{\circ}\text{F.}$ in the central 2 in. and $\pm 3^{\circ}\text{F.}$ in the central 3 inches.

LOAD AND EXTENSION MEASUREMENT

Load measurement during tensile tests was obtained through the use of a steel proving ring in series with the specimen.

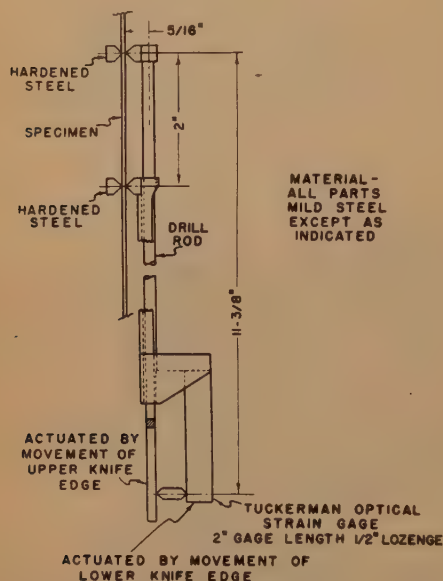


FIG. 4.—SCHEMATIC DRAWING OF EXTENSOMETER ASSEMBLY FOR USE AT ELEVATED TEMPERATURES.

Deformation of the ring under load was indicated by a pair of SR-4 A-11 electric strain gauges mounted in opposition on the inner and outer surfaces of the ring. Previous calibration allowed expression of the strain-gauge readings in terms of load. The maximum error in load readings in the range employed is thought to be no more than 5 lb. The use of two gauges separated only by the thickness of the proving ring (and, therefore, at nearly equivalent temperatures) allowed omission of the "dummy" gauge generally required with a single SR-4 gauge to secure temperature compensation.

In the tests at room temperature, a Tuckerman optical strain gauge was used to obtain measurements of extension. It operated over a 2-in. gauge length with a lozenge distance of $\frac{1}{2}$ inch.

In the elevated-temperature tests, a similar Tuckerman strain gauge positioned outside the furnace was actuated by extension arms, which were attached to the specimen by means of knife edges. Extension of the 2-in. gauge length was thus indicated by the external Tuckerman gauge. Details of the elevated-temperature extensometer are furnished in Figs. 3 and 4.

For strain measurements at all temperatures, extensometers were employed on only one side of the specimen. Conditions of initial bending, therefore, were not compensated, with the result that reliable stress-strain relations were not obtained at stresses up to about 2500 lb. per sq. in. This, however, did not constitute a serious problem, since straight-line relationships were obtained at stresses higher than 2500 lb. per sq. in., allowing extrapolation to the zero value.

Often it was necessary during the course of a test to stop the tensile machine and to reset the Tuckerman gauge. This was required because the range with a single setting was not sufficient to reach the condition defining the tensile yield stress where this stress was greater than about 45,000 lb. per sq. in. Such resetting was done at low stresses, with the result that no changes in load were observed during the resetting interval.

A careful calibration of the elevated-temperature extensometer was made at atmospheric temperature. It indicated an error of less than 1 per cent in strain measurements. The calibration in which the elevated-temperature extensometer was checked against another Tuckerman optical strain gauge was not absolute, since the manufacturer's original calibration was employed for the latter.

VARIATION OF STRAIN RATE

All tests were conducted at a constant crosshead speed of 0.06 in. per min. The rate of strain in the 2-in. gauge length, however, varied considerably in the course

of a test, the rate in the elastic portion being much lower than that attained in the plastic region.

remainder of the specimen was well below the elastic limit. Thus an increasing proportion of the crosshead motion was con-

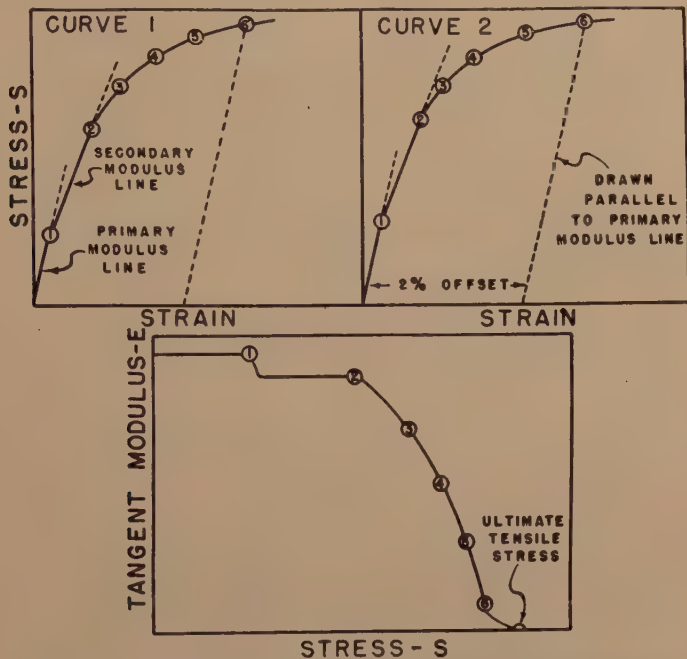


FIG. 5.—DERIVATION OF AVERAGE TANGENT MODULUS CURVE FROM STRESS-STRAIN CURVES FOR TWO TENSILE TESTS.

Steps in derivation:

A. Selection of representative points on curves I and II.

1. Points 1, 2, 6 are selected on each curve as follows:
1 is the intersection of primary and secondary modulus lines.
2 is the point of departure from the secondary modulus line.
6 is the yield strength (0.2 per cent offset as shown).

2. Points 3, 4, 5 lying between 2 and 6 are selected arbitrarily on curve I and the corresponding points on curve II are selected so that $\frac{S_{II}}{S_{II_6}} = \frac{S_I}{S_{I_6}}$.

B. Measurement of values S and E for points 1 to 6 on each curve.

C. Plotting of the tangent modulus curve using at each point the average values $\frac{E_I + E_{II}}{2}$

$$\text{and } \frac{S_I + S_{II}}{2}.$$

This variation may be attributed in part to the specimen design. In the early stages of a test, both the reduced section and the much longer grip section were strained elastically, so that only a small portion of the crosshead motion was concentrated in the gauge length. Because of its smaller cross section, however, the reduced section yielded plastically at loads at which the

concentrated in the gauge length after the yield stress had been reached.

Actual values of the observed strain rates are as follows for several conditions:

Stress	$\frac{1}{4}$ Hr. at 212°F.	1000 Hr. at 375°F.
Zero stress to yield stress.....	0.0028	0.0046
Yield stress to fracture.....	0.019	0.026
Zero stress to fracture.....	0.014	0.021

These refer to the 2-in. gauge length, expressed as inch per inch per minute, and are average rates for all materials.

cases the relation between stress and the slope of the curve is a significant feature.^{8,9,10} The slope is often called the

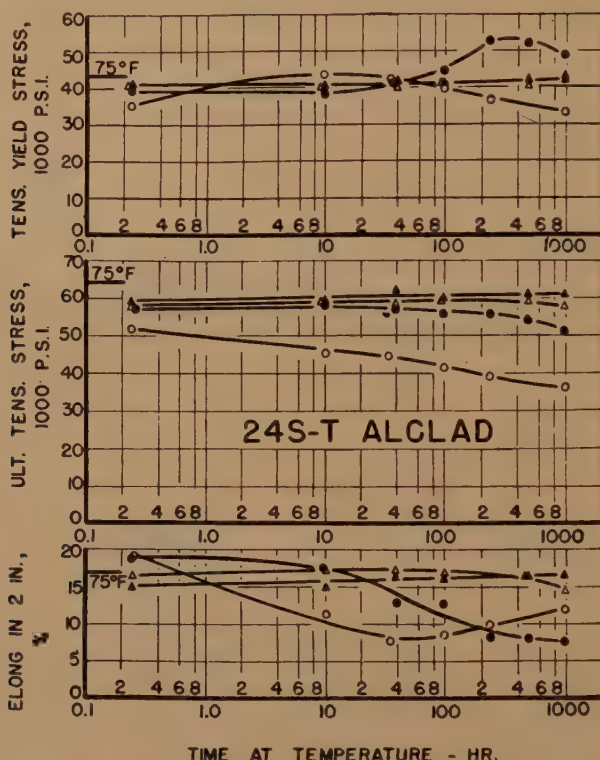


Fig. 6. Alclad 24S-T sheet. Sheet thickness, 0.040 in.; direction of stress, cross grain; crosshead speed, 0.06 in. per minute.

FIGS. 6-9.—EFFECT OF TEMPERATURE AND TIME OF EXPOSURE ON ELEVATED-TEMPERATURE TENSILE PROPERTIES.

▲ 212°F.
△ 250°F.
● 300°F.
○ 375°F.
(Each point represents average value of two or more tests.)

DETERMINATION OF TENSILE YIELD STRESS AND DERIVATION OF TANGENT MODULUS CURVES

Values of tensile yield stress were obtained by means of the 0.2 per cent offset method, the offset line being drawn parallel to that straight portion of the stress-strain curve corresponding to the primary modulus.

In certain types of design, especially when buckling must be considered, it is desirable to know the shape of the stress-strain curve in the plastic region. In such

"tangent modulus" and the curve representing it as a function of stress is known as a "tangent modulus curve." The latter is essentially equivalent to the stress-strain curve itself, since either type may be constructed directly from the other.

Although the tangent modulus curves presented in this paper were derived from tensile data, they may be useful as first approximations to the corresponding compressive values generally desired for design purposes. A comparison of such curves in tension and compression for

several aluminum-alloy sheet materials at room temperature is shown by Templin, Hartman and Paul.¹¹

tensile yield stress, and elongation in two inches. In general, each point on these curves is an average value based upon two

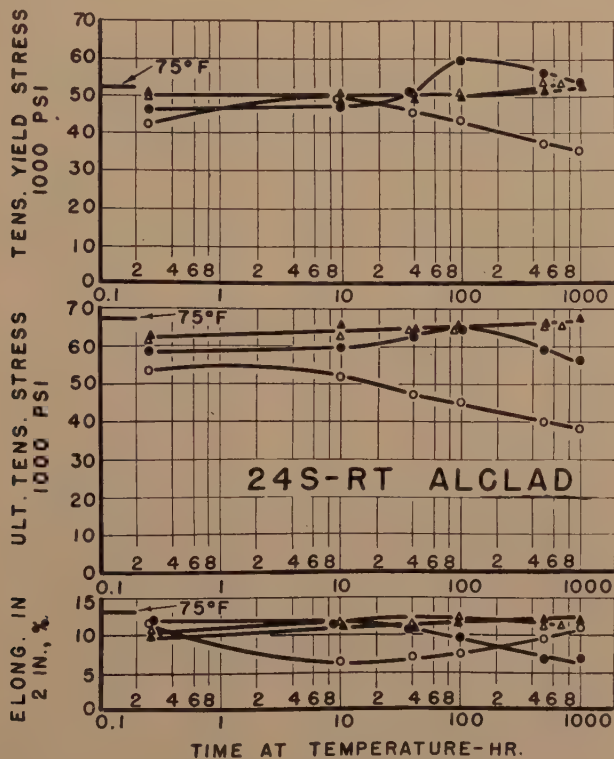


Fig. 7. Alclad 24S-RT sheet. Sheet thickness, 0.064 in.; direction of stress, cross grain; cross-head speed, 0.06 in. per minute.

The curves of the present paper were derived in the following manner. A series of tangents was drawn to each of the individual stress-strain curves. The slopes of the tangents were then measured and plotted against the corresponding stresses and smooth curves were faired in to connect the points. Fig. 5 describes the method used in averaging the tangent modulus data obtained in duplicate tests.

EXPERIMENTAL RESULTS

Test results are shown by means of curves in Figs. 6 to 21. Figs. 6 to 13 show the effects of testing temperature and exposure time on ultimate tensile stress,

or more tests. Values of the tangent modulus are plotted against stress in Figs. 14 to 21. These latter figures also indicate the effect of temperature on the primary and secondary moduli of elasticity, the values of which appeared to be independent of the time at temperature.

TENSILE PROPERTIES AT ELEVATED TEMPERATURES

The effects of time and temperature on the tensile properties of the various materials are shown in Figs. 6 to 13. The changes in properties are of two types:

1. Those produced by the effect of temperature alone, independent of attendant precipitation effects. followed in some cases by overaging (Figs. 6, 7 and 8). The tensile properties of 24S-T and 24S-RT are little affected by

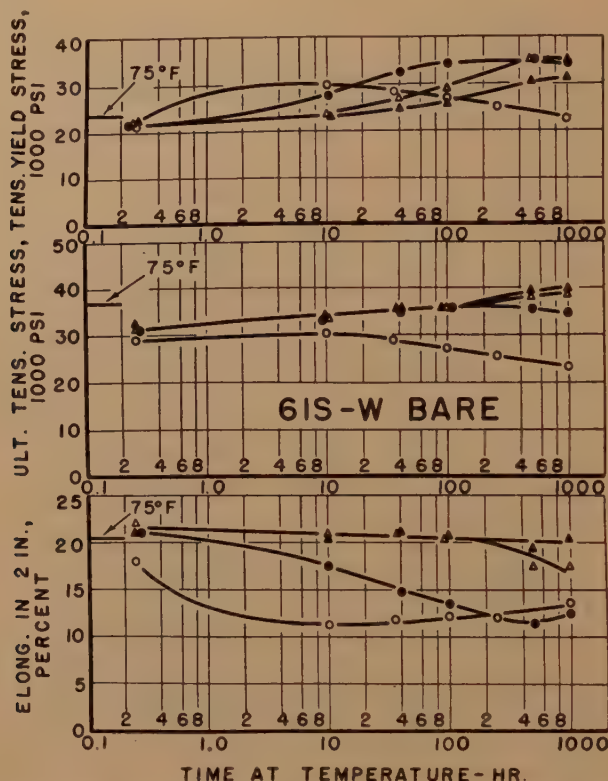


Fig. 8. Bare 61S-W sheet. Sheet thickness, 0.040 in.; direction of stress, cross grain; crosshead speed, 0.06 in. per minute.

2. Those resulting from structural changes in the material induced by elevated-temperature exposure.

In the case of the shortest exposure time ($\frac{1}{4}$ hr.), the principal effect is that of temperature alone, increases in temperature producing lower values of yield stress and ultimate stress. With continued exposure, especially at the higher temperatures, structural changes occur and the materials of groups A and B behave in dissimilar manners.

The effects noted in the specimens of group A (24S-T, 24S-RT and 61S-W) are those of marked precipitation-hardening

exposures of as much as 1000 hr. at 212° and 250°F . At 300°F . there is a substantial increase in yield stress with eventual overaging, whereas early overaging is apparent at 375°F . Even at the latter temperature, the yield stress after 1000 hr. is scarcely lower than the $\frac{1}{4}$ -hr. value. A marked drop however, is noted in ultimate tensile stress. In the 61S-W material, similar trends are apparent but precipitation effects are more prominent at the lower temperatures.

Since the materials of group B have been subjected to previous artificial aging, the effects are generally those of overaging.

Figs. 9 to 13 indicate no appreciable decreases in yield stress during continued exposure at temperatures as high as 250°F.; i.e., the values after 1000 hr. are similar

materials, the former having a relatively low yield stress. Secondary moduli were observed in all clad materials except where prolonged exposure at elevated tem-

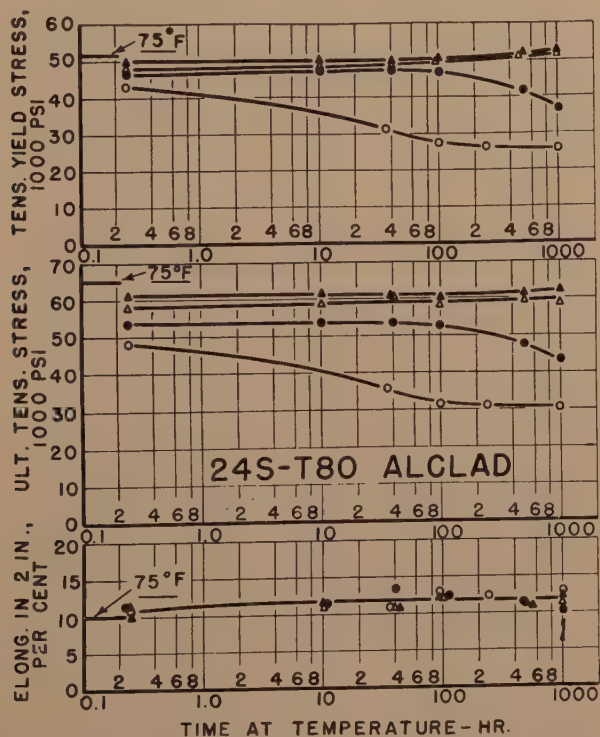


Fig. 9. Alclad 24S-T80 sheet. Sheet thickness, 0.040 in.; direction of stress, cross grain; cross-head speed, 0.06 in. per minute.

to the $\frac{1}{4}$ -hr. values. In each case, however, there are considerable decreases in both yield stress and ultimate stress at 375°F. and smaller decreases at 300°F. As might be expected, the greatest loss of strength occurs in XB75S-T, which has the lowest temperature for artificial aging (p. 199).

PRIMARY AND SECONDARY MODULI AT ELEVATED TEMPERATURES

As is well known, the occurrence of a secondary modulus of elasticity in clad aluminum alloys is due to the dissimilar characteristics of the cladding and core

materials, the former having a relatively low yield stress. Secondary moduli were observed in all clad materials except where prolonged exposure at elevated tem-

perature had caused a large decrease in the yield stress of the core material. In such cases the secondary modulus was poorly defined or was entirely absent. Values of the primary and secondary moduli decrease with increasing temperature (Figs. 14 to 21). The data summarized in Table 3 have been treated as dependent on temperature alone, since no effect of exposure time was noted. The latter observation is not unexpected, since it has been observed that on a given alloy at room temperature the modulus of elasticity does not vary greatly for the various metallurgical conditions attain-

able. Thus the moduli of 24S-O, 24S-T, 24S-T86, etc., are approximately the same at room temperature. By analogy, continued exposure at elevated temperature

ed at the lower temperatures and single curves have been drawn to represent all times from $\frac{1}{4}$ hr. to 1000 hr. At the higher temperatures, where time is a factor.

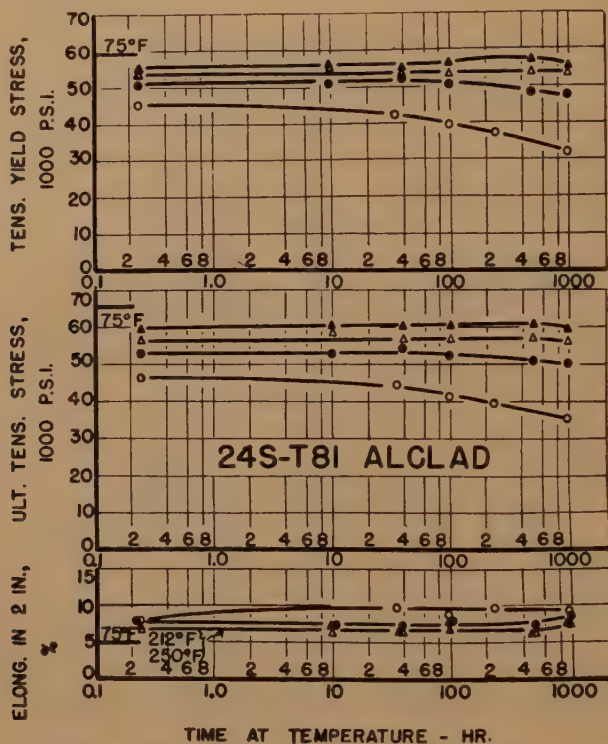


FIG. 10. Alclad 24S-T81 sheet. Sheet thickness, 0.040 in.; direction of stress, cross grain; cross-head speed, 0.06 in. per minute.

FIGS. 10-13.—EFFECT OF TEMPERATURE AND TIME OF EXPOSURE ON ELEVATED-TEMPERATURE TENSILE PROPERTIES.

▲ 212°F.
△ 250°F.

● 300°F.
○ 375°F.

(Each point represents average value of two or more tests.)

may be expected to have little effect on values of the elastic moduli in spite of the fact that extensive metallurgical changes may be occasioned.

TANGENT MODULUS CURVES AT ELEVATED TEMPERATURES

The effects of temperature and time on the tangent modulus curves are shown in Figs. 14 to 21. Here the relatively minor effects of exposure time have been neglect-

families of curves are obtained. The intermediate curves of such families have been omitted in Figs. 14 to 21 for the sake of clarity and only the more important curves have been presented. In each instance the extremes have been included (that is, the tangent modulus curves falling farthest to the right and to the left).

As noted previously, the initial, horizontal portions of the curves (the primary and secondary moduli) are in all cases determined by temperature alone.

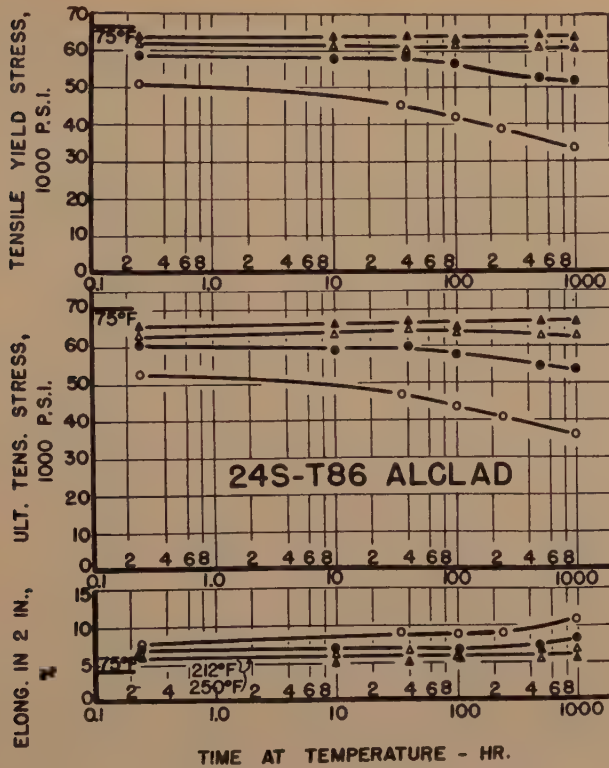


Fig. 11. Alclad 24S-T86 sheet. Sheet thickness, 0.040 in.; direction of stress, cross grain; cross-head speed, 0.06 in. per minute.

TABLE 3.—Effect of Temperature on the Modulus of Elasticity in Tension at Elevated Temperatures^a

Material	Modulus	Temperature				
		75°F.	212°F.	250°F.	300°F.	375°F.
24S-T Alclad....	Primary	10.4	9.6	9.6	9.4	9.2
	Secondary	9.2	8.7	8.7	8.5	7.9
24S-RT Alclad..	Primary	10.6	10.2	10.1	9.8	9.2
	Secondary	9.7	9.2	9.2	8.8	8.1
61S-W (bare)...	Primary	9.9	9.1	9.1	8.9	8.3
	Secondary					
24S-T80 Alclad..	Primary	9.9	9.4	9.4	9.2	8.7
	Secondary	9.0	8.8	8.6	8.4	8.0
24S-T81 Alclad..	Primary	10.4	9.7	9.6	9.7	9.1
	Secondary	9.3	8.9	8.8	8.6	8.1
24S-T86 Alclad..	Primary	10.3	9.7	9.7	9.5	8.6
	Secondary	9.1	8.9	8.7	8.4	7.6
61S-T (bare)....	Primary	10.1	9.3	9.2	8.8	8.3
	Secondary					
XB75S-T Alclad	Primary	9.9	9.3	9.2	8.9	8.2
	Secondary	8.8	8.5	8.4	7.8	

^a Each value listed is an average based on exposure times ranging from $\frac{1}{4}$ hr. to 1000 hr. The original data reveal no dependency on exposure time.

THE PROBLEM OF CREEP

As with other materials, creep may be a significant factor in elevated-temperature applications where aluminum alloys sustain loads for long periods. Stress-rupture tests at 300° and 375°F. recently completed at the University of California indicate that eventual failure by rupture may occur under steady loading at stresses well below the value of the short-time "tensile yield stress." For this reason tensile data derived at the higher temperatures should be used with caution in design. This applies in connection with tangent modulus, yield stress, and ultimate stress.

CORROSION RESISTANCE

In a consideration of aluminum alloys for use at elevated temperatures the

problem of corrosion resistance may require attention.

Considerable information is available on the effects of prior artificial aging on

yield stress (Fig. 6 and 7). It seems probable that such difficulties may be minimized through use of the 24S-T8 series in preference to 24S-T and 24S-RT. As in

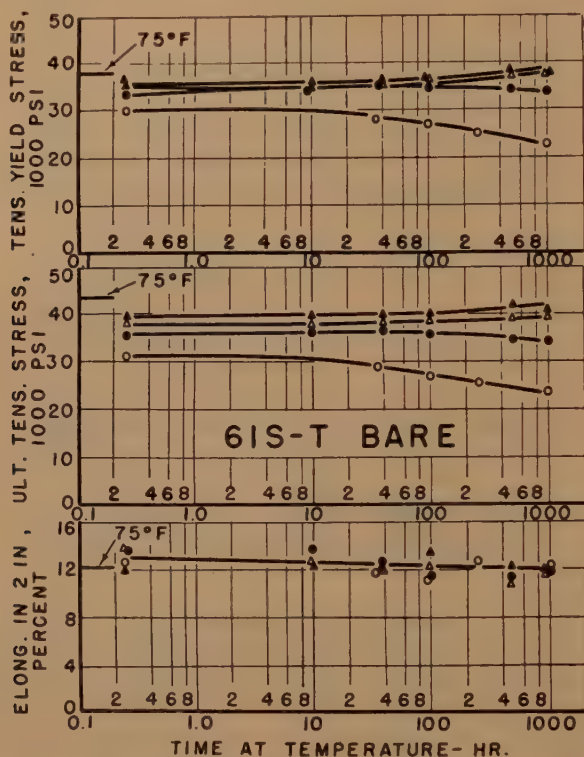


Fig. 12. Bare 61S-T sheet. Sheet thickness, 0.040 in.; direction of stress, cross grain; cross-head speed, 0.06 in. per minute.

corrosion resistance at room temperature. In 24S-T and 24S-RT, a marked increase in susceptibility is known to occur in the early stages of elevated-temperature aging. With continued aging, corrosion resistance improves and approaches that of the original material. It appears that the aging time needed for optimum resistance coincides with that required for attainment of maximum yield stress.^{1,5} As a consequence, corrosion problems may be expected to attend the use of 24S-T and 24S-RT at elevated temperatures up to about 300°F., for under such conditions considerable time is required for attainment of maximum

the 24S-T8 series, the corrosion resistance of artificially aged XB75S and 61S has been found adequate after the period required to attain maximum yield stress. In this respect, XB75S-T and 61S-T may also be suitable for elevated-temperature service.

The preceding remarks refer to the problem of room-temperature corrosion following elevated-temperature exposure. It is possible that susceptibility to corrosion at elevated temperatures, especially in unfavorable atmospheres, may be greater than indicated by tests performed at room temperature.

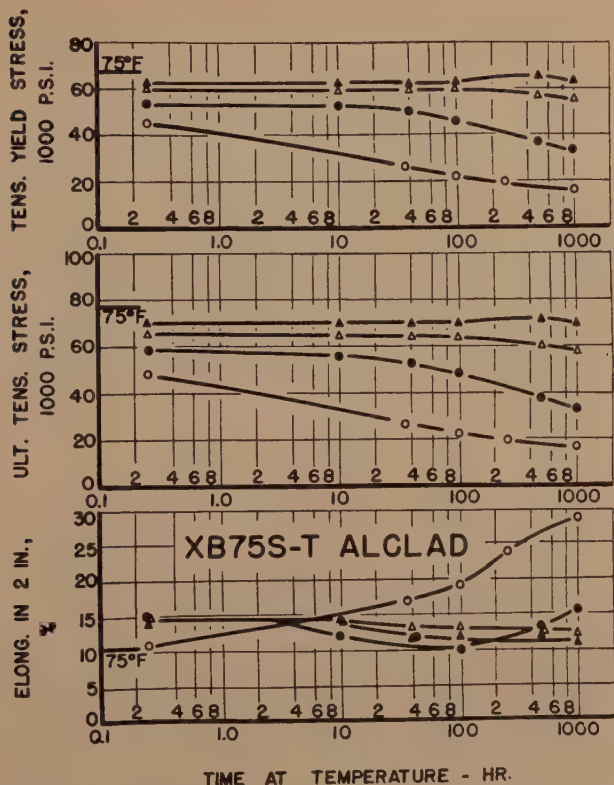


Fig. 13. Alclad XB75S-T sheet. Sheet thickness, 0.040 in.; direction of stress, cross grain; crosshead speed, 0.06 in. per minute.

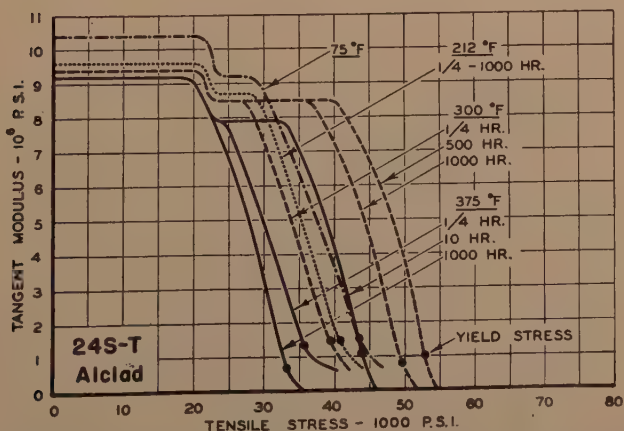


Fig. 14. 24S-T Alclad sheet. Sheet thickness, 0.040 in.; direction, cross grain.

FIGS. 14-17.—EFFECTS OF TEMPERATURE AND EXPOSURE TIME ON THE TANGENT MODULUS AT ELEVATED TEMPERATURES.

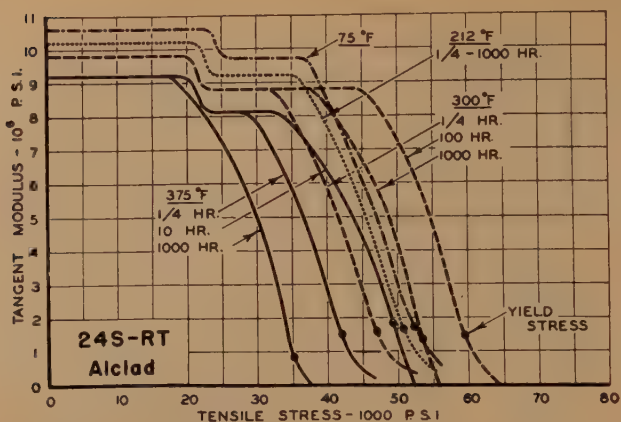


Fig. 15. 24S-RT Alclad sheet.

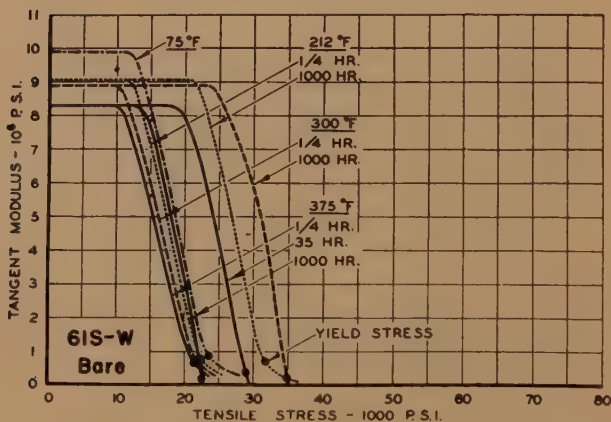


Fig. 16. 61S-W bare sheet.

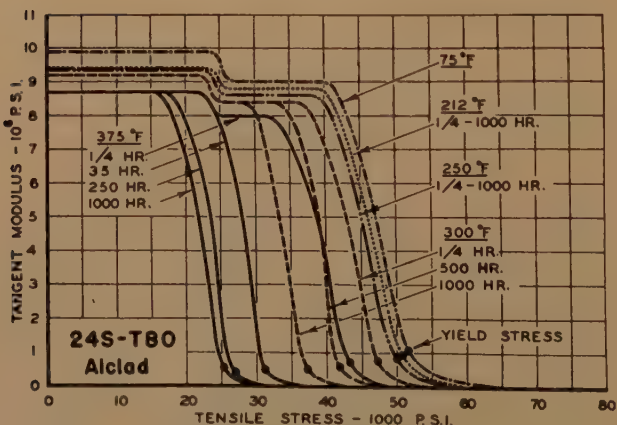


Fig. 17. 24S-T80 Alclad sheet.

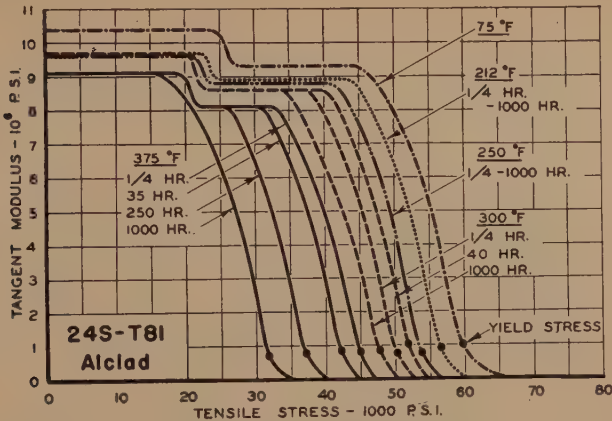


Fig. 18. 24S-T81 Alclad sheet.

FIGS. 18-21.—EFFECTS OF TEMPERATURE AND EXPOSURE TIME ON THE TANGENT MODULUS AT ELEVATED TEMPERATURES.

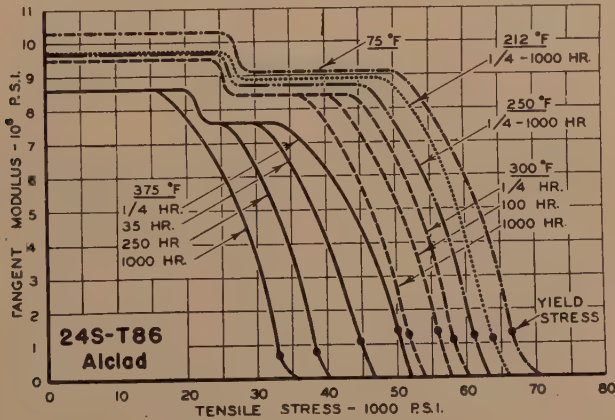


Fig. 19. 24S-T86 Alclad sheet.

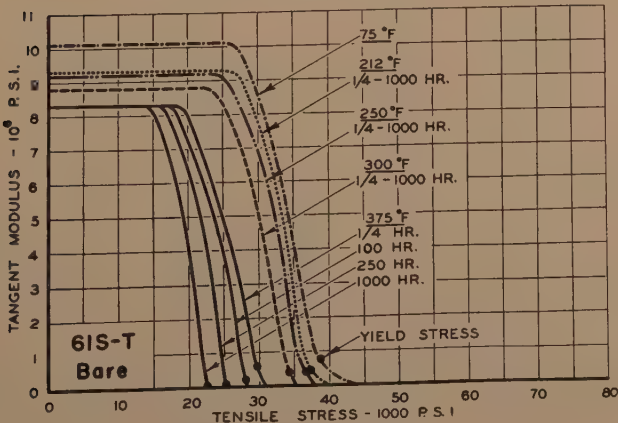


Fig. 20. 61S-T bare sheet.

CHOICE OF MATERIALS FOR ELEVATED TEMPERATURE SERVICE

On the basis of the foregoing tensile data and the remarks on corrosion it is possible

to judge the materials with regard to suitability for service at elevated temperatures within the range investigated.

2. Of the materials tested, the 24S-T8 series appears to offer the best possibilities

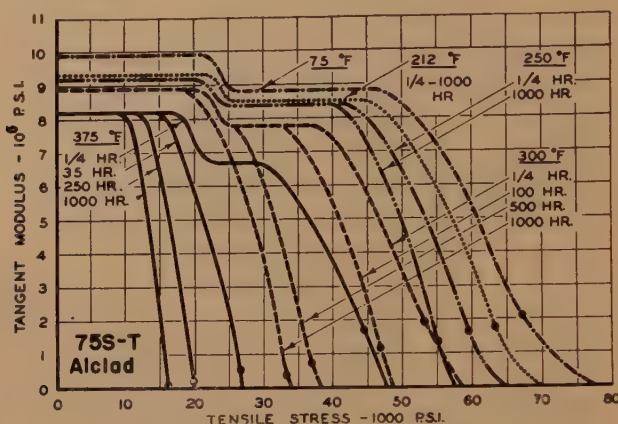


Fig. 21. XB75S-T Alclad sheet.

to judge the materials with regard to suitability for service at elevated temperatures within the range investigated. It would seem that members of the 24S-T8 series offer the best possibilities.

After sufficiently long exposure, 24S-T and 24S-RT may approach the strength of the 24S-T8 series, but until fully aged they are lower in strength and may be expected to be more susceptible to corrosion. The strengths of 61S-W and 61S-T are lower than those of the 24S-T8 series under all conditions tested, while XB75S-T suffers a rapid loss of strength at temperatures above 250°F.

At the higher temperatures creep may be a problem and should be considered regardless of the material selected.

SUMMARY AND CONCLUSIONS

1. The elevated-temperature tensile properties of eight high-strength aluminum-alloy sheet materials have been determined. Temperatures from 75° to 375°F. were employed with exposure times ranging up to 1000 hr. at tempera-

ture. The effects of these variables on the tangent modulus have also been reported.

3. As with other materials, tensile data obtained for aluminum alloys at elevated temperatures should be used with care. At the higher temperatures creep may become a significant factor and eventual failure by rupture may occur under steady loading at stresses well below the short-time "tensile yield stress."

ACKNOWLEDGMENT

The authors wish to express their appreciation to the following agencies and associates who were responsible for the initiation and fulfillment of the testing program:

1. The Office of Production Research and Development and the War Metallurgy Committee for sponsorship and guidance.

2. The Research and Testing Panel of the Aircraft War Production Council, Hollywood, Calif., for direction and criticism.

3. The Lockheed Aircraft Corporation of Burbank, Calif., for preparation of specimens.

4. The engineers and technicians who, in addition to the authors, were engaged in the program; namely, Frank Brezee, Bernard P. Faas, Woodrow Harper, James T. Lapsley, Allan T. Robinson and Barbara Roney.

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DISCUSSION

(A. H. Geisler presiding)

E. H. BURKART.*—The information on the tensile properties of aluminum alloys at elevated temperatures, as presented by the authors of the subject paper, is a valuable contribution. These data have been found particularly useful in the design of airplane wing and empennage structures incorporating thermal de-icing.

Aside from the suggestion that this work be supplemented by a limited investigation of the effect of temperature on the compressive properties, we have no technical comment to make at this time.

A. E. FLANIGAN (author's reply).—The authors are pleased to receive the comments of Mr. Burkart, who was an active participant in planning the investigation. The compressive properties of aluminum-alloy sheet at materials have been the subject of a subsequent investigation. The results will be published at an early date.

*Lockheed Aircraft Corporation, Burbank, California.

Correlation of Mechanical Properties and Corrosion Resistance of 24S-type Aluminum Alloys as Affected by High-temperature Precipitation

BY W. D. ROBERTSON,* JUNIOR MEMBER A.I.M.E.

(New York Meeting, October 1945)

A considerable quantity of experimental data is available on the effect of time, temperature, work-hardening and composition on the mechanical properties and corrosion resistance of aluminum alloys. There is, however, little unity of purpose or generality in most of the studies and, because the number of variables is large, the results often are not applicable to the problems that arise in practice. Furthermore, the customary expression of the effect of different variables as separate curves or as three-dimensional diagrams with time, temperature and the dependent variables as coordinates, renders the task of selecting the optimum time and temperature of precipitation treatment, with respect to their simultaneous but unequal effect on the various properties, exceedingly difficult.

The introduction of precipitation treatments to raise the yield strength of 24S-type alloys has created a need for a method of correlating and summarizing the effect of time and temperature on the mechanical properties and susceptibility to intercrystalline corrosion. Correlation is particularly desirable because the choice of time and temperature is of necessity a compromise to achieve the best possible combination of properties, and the optimum conditions cannot be accurately specified

unless the data are in a form in which the alternatives can be readily compared.

Therefore, the work described here was undertaken to find a common relationship that would be capable of expressing the effect of precipitation time and temperature on the various properties and by means of which the relative effects could be correlated and their interpretation facilitated.

REVIEW OF PREVIOUS WORK

In connection with an investigation of the interrelation of age-hardening and creep performance of nickel-silicon-copper alloys, Jenkins and Bucknall¹ demonstrated that the time required to attain maximum hardness and tensile strength could be expressed by a relationship of the form:

$$t = K \cdot 10^{m/T} \quad (1)$$

where t is the time in hours and T the temperature of aging, expressed in degrees absolute, and m and K are constants. They also pointed out that this expression is analogous to that which describes the change of the diffusion coefficient D with temperature; namely,

$$D = Ae^{-Q/RT} \quad (2)$$

Later, Cohen used this relationship in studies of the mechanism of age-hardening of a silver-rich copper alloy² and of duralumin.³

Manuscript received at the office of the Institute May 21, 1945. Issued as T.P. 1934 in METALS TECHNOLOGY, October 1945.

* Head of Chemical Metallurgy Division, Aluminium Laboratories Limited, Kingston, Ont., Canada.

¹ References are at the end of the paper.

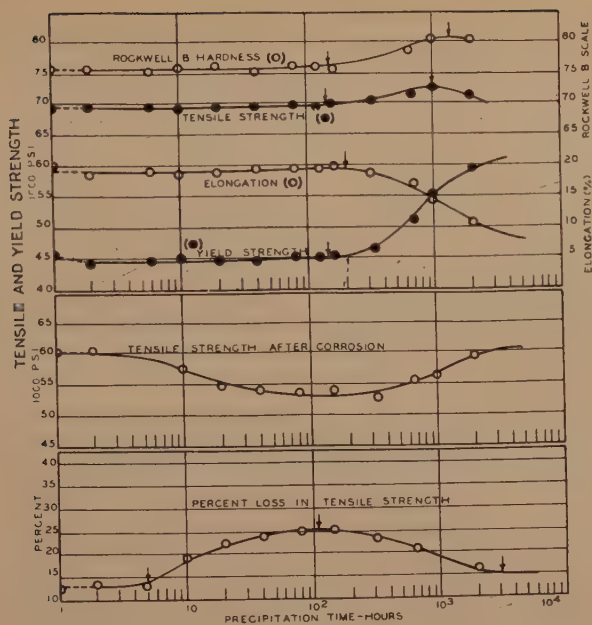


FIG. 1.—PRECIPITATION AT 130°C.

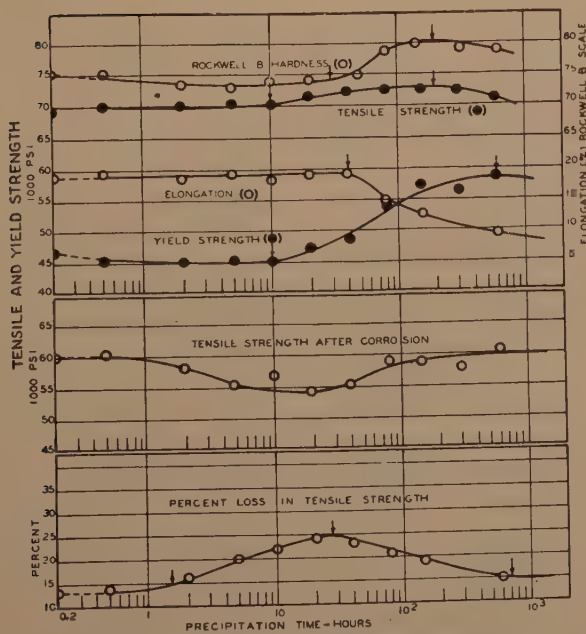


FIG. 2.—PRECIPITATION AT 145°C.

FIGS. 1-2.—INFLUENCE OF PRECIPITATION HEAT-TREATMENT CONDITIONS ON MECHANICAL PROPERTIES AND CORROSION CHARACTERISTICS OF 24S-T.

In the work of Jenkins and Bucknall, the illustrations of the application of their expression were limited to the attainment of maximum tensile strength and resistivity. Cohen carried the application, with respect to hardness, a step further by demonstrating that the progressive stages in the hardening process could each be represented by the same expression, and that two of the three stages in the hardening process were related to characteristic grain-boundary precipitation and general precipitation within the grains.

Thus, it should be possible to express the effect of precipitation time and temperature on the corrosion resistance in a similar manner. This follows from the fact that age-hardenable alloys become susceptible to intercrystalline corrosion as a consequence of localized precipitation at the grain boundaries of one or more phases from solid solution, which creates a potential difference between the grains and their boundaries;⁴ and also that the local potential difference, starting at zero for the solid solution, increases to a maximum and declines to zero again as the alloy is aged at elevated temperatures.⁵ Presumably, then, the rising potential difference results from progressive grain-boundary precipitation and the return to zero represents the completed general precipitation, which eliminates the local concentration gradient between the grains and their boundaries, and with it the source of the potential difference.

This being so, there is a single expression governing the mechanical and the "electrochemical" properties, and consequently it is possible to express both in the same terms.

The experimental work described in the following pages is devoted to a demonstration of this hypothesis and to illustrating the utility of the method as a means of expressing a variety of data in a convenient form.

EXPERIMENTAL PROCEDURE

The alloy used for this investigation was commercial 24S sheet, 0.057 in. thick and of the following composition: Cu, 4.55 per cent; Fe, 0.24; Mg, 1.50; Mn, 0.66; Si, 0.15; Ti, 0.01.

The sheet was received in the room-temperature aged condition. It was sheared into strips one inch wide, parallel to the direction of rolling, and solution-heat-treated in a salt bath at 495°C. for 30 min., quenched in less than one second in water at 22°C. and aged at room temperature for a period exceeding two weeks. The strips were heat-treated in lots of 50 and were shuffled to average out any variation between the lots.

The precipitation heat-treatments, following complete room-temperature aging, were carried out in air ovens for periods exceeding one hour; for shorter periods, a salt bath was used and the specimens were quenched in water to ensure control over the time at temperature. Temperature control in both cases was $\pm 1^\circ\text{C}$.

The mechanical properties were obtained in the customary manner from the average of four specimens for each point, and the corresponding properties after corrosion from the average of eight specimens, all of which were precipitation-treated at the same time. The Rockwell B hardness values ($\frac{1}{16}$ -in. ball and 100-kg. load) represent the average of four values taken not less than one month after completion of the precipitation treatment in question.

The corrosion test was conducted by periodic immersion of the specimens in a 5 per cent solution of sodium chloride to which 0.3 per cent hydrogen peroxide had been added. The specimens were stressed to a maximum fiber stress of 80 per cent of their tensile yield strength during the test, by bending them in an arc between the ends of special porcelain holders. After 48 hr. the specimens were removed and machined to tensile test bars, and their

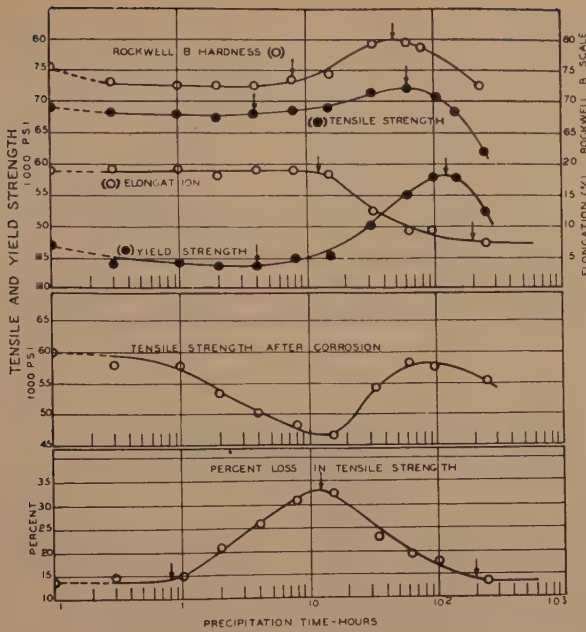


FIG. 3.—PRECIPITATION AT 160°C.

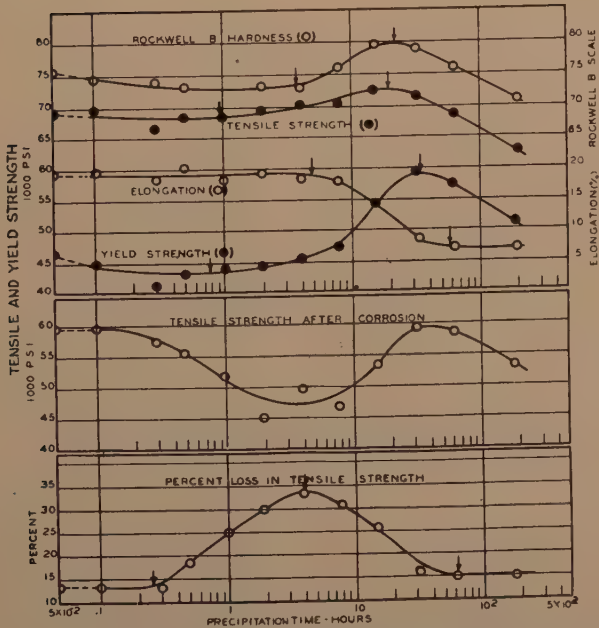


FIG. 4.—PRECIPITATION AT 175°C.

FIGS. 3-4.—INFLUENCE OF PRECIPITATION HEAT-TREATMENT CONDITIONS ON MECHANICAL PROPERTIES AND CORROSION CHARACTERISTICS OF 24S-T.

remaining mechanical properties were determined for comparison with those obtained from the corresponding uncorroded specimens. Since the emphasis in this investigation is on the shift of values with respect to precipitation time and temperature, and the absolute figures have no significance, the details of procedure have been omitted. However, a full discussion of the apparatus and testing method is available in the *Canadian Journal of Research*.⁶

EXPERIMENTAL RESULTS

Figs. 1 to 6 show the curves of ultimate tensile strength, yield strength (0.2 per cent offset), elongation in 2 in. and Rockwell B hardness for each precipitation temperature from 130° to 205°C. The corresponding tensile strength after corrosion and the percentage loss in tensile strength are also shown in the figures. The points at the extreme left were obtained after completed room-temperature aging and that part of the curve is dotted to emphasize the change in scale.

The curves of percentage loss in tensile strength have been drawn from the smoothed curves of initial and final tensile strength. In all cases smooth curves have been drawn on the assumption of continuous variation. When more than one possibility existed, that which best maintained the apparent similarity of form of the curves was chosen as the most probable course.

The points marked by arrows on each set of isothermal curves have been re-plotted in Fig. 7 to verify the exponential expression, which has been put in the form of a linear equation for convenient verification; thus,

$$\log t = \frac{m}{T} + \log K \quad [3]$$

is equivalent to Eq. 1, where t is the time required to attain the stated property at a temperature T , expressed in degrees absolute, and m and K are constants. A plot of

$\log t$ vs. $1/T$ should be a straight line if the expression represents the experimental data. The parameters m and K have been calculated from the slope of the straight lines in Fig. 7 and are given in Table 1, together with the corresponding values of Q in the analogous diffusion equation (Eq. 2). The latter is equal to the slope m multiplied by the product of the gas content R and the Napierian base

$$(R \times e = 4.58).$$

TABLE 1.—Parameters m and K in Relationship $t = K \cdot 10^{m/T}$

Property Represented	m	K	Apparent Heat of Diffusion Q , Cal. per Gram Atom
Maximum tensile strength.....	$6.6 \cdot 10^3$	$3.72 \cdot 10^{-14}$	30,400
Maximum yield strength.....	$7.9 \cdot 10^3$	$7.40 \cdot 10^{-17}$	36,200
Maximum hardness....	$6.6 \cdot 10^3$	$3.72 \cdot 10^{-14}$	30,400
Initial increase in tensile strength.....	$6.6 \cdot 10^3$	$2.24 \cdot 10^{-15}$	30,400
Initial increase in yield strength.....	$6.6 \cdot 10^3$	$2.24 \cdot 10^{-15}$	30,400
Initial increase in hardness.....	$6.6 \cdot 10^3$	$5.0 \cdot 10^{-18}$	30,400
Initial decrease in elongation.....	$5.77 \cdot 10^3$	$7.08 \cdot 10^{-13}$	26,400
Attainment of minimum elongation....	$7.9 \cdot 10^3$	$1.23 \cdot 10^{-18}$	36,200
Initial decrease in corrosion resistance (grain-boundary precipitation).....	$5.1 \cdot 10^3$	$1.20 \cdot 10^{-12}$	23,400
Minimum corrosion resistance.....	$5.9 \cdot 10^3$	$2.51 \cdot 10^{-13}$	27,000
Return to initial corrosion resistance (completion of general precipitation).....	$6.6 \cdot 10^3$	$1.20 \cdot 10^{-13}$	30,400

The appearance and progress of intercrystalline attack resulting from precipitation heat-treatment was followed by microscopic examination of the corroded specimens. A representative selection is shown in Fig. 8, which is a reproduction from Fig. 4 of the curve of loss in tensile strength after precipitation at 175°C.

All the curves of mechanical properties are similar, and consist of an initial drop followed by a more or less rapid rise to a maximum and a final decrease in the range

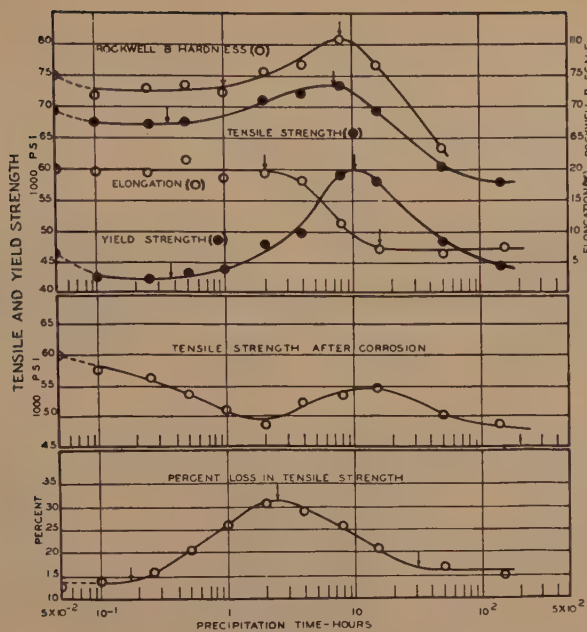


FIG. 5.—PRECIPITATION AT 190°C.

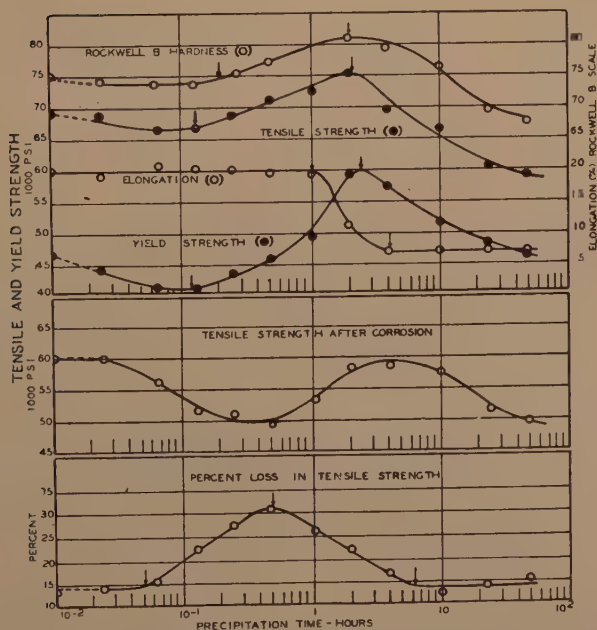


FIG. 6.—PRECIPITATION AT 205°C.

FIGS. 5-6.—INFLUENCE OF PRECIPITATION HEAT-TREATMENT CONDITIONS ON MECHANICAL PROPERTIES AND CORROSION CHARACTERISTICS OF 24S-T.

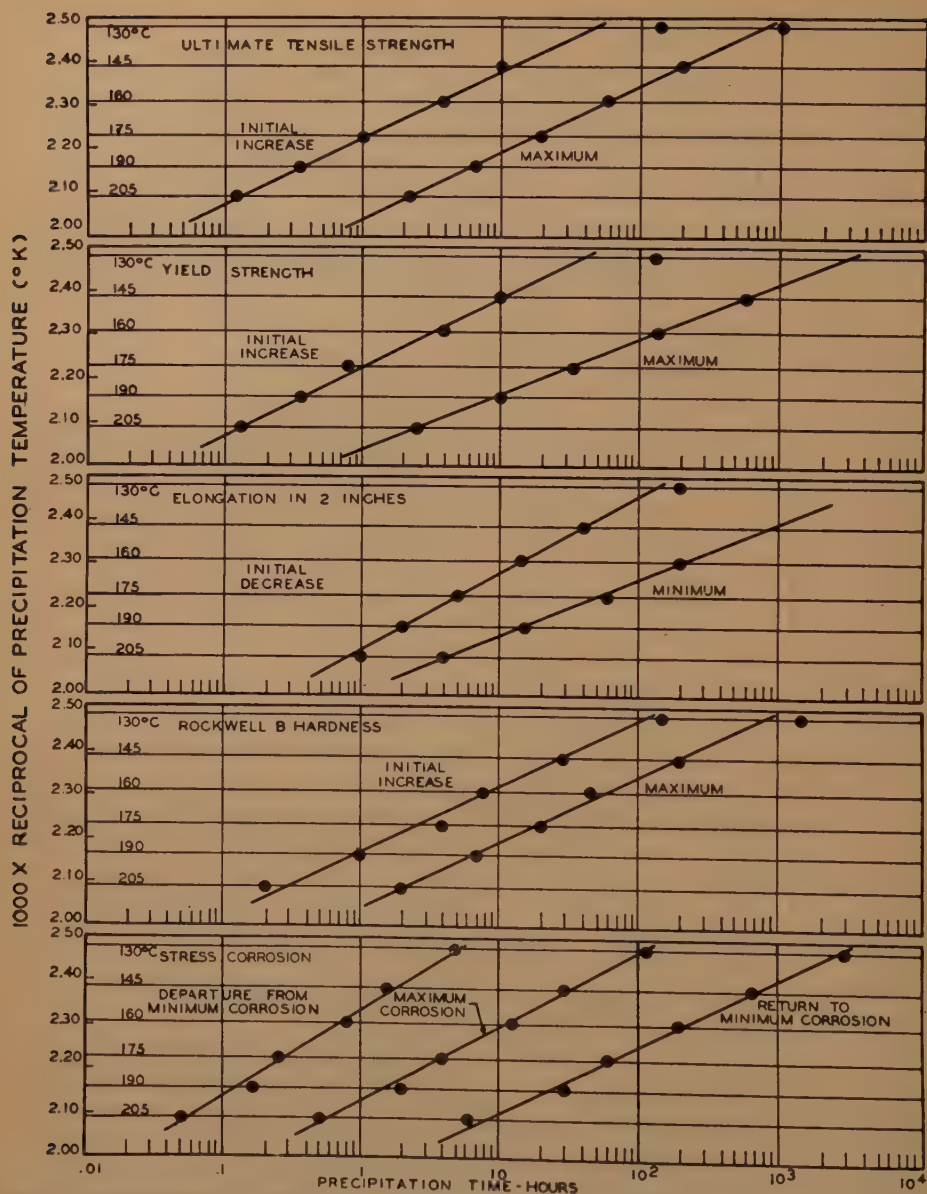


FIG. 7.—CORRELATION OF MECHANICAL PROPERTIES AND CORROSION RESISTANCE OF 24S-T AS AFFECTED BY PRECIPITATION TREATMENT.

known as "overaging." The curves of percentage loss in tensile strength, however, when plotted on a logarithmic scale, show three distinct sections: one in which

returns to a point very near the initial value, and remains constant thereafter, indicates that the reaction (precipitation) is complete. This question will be re-

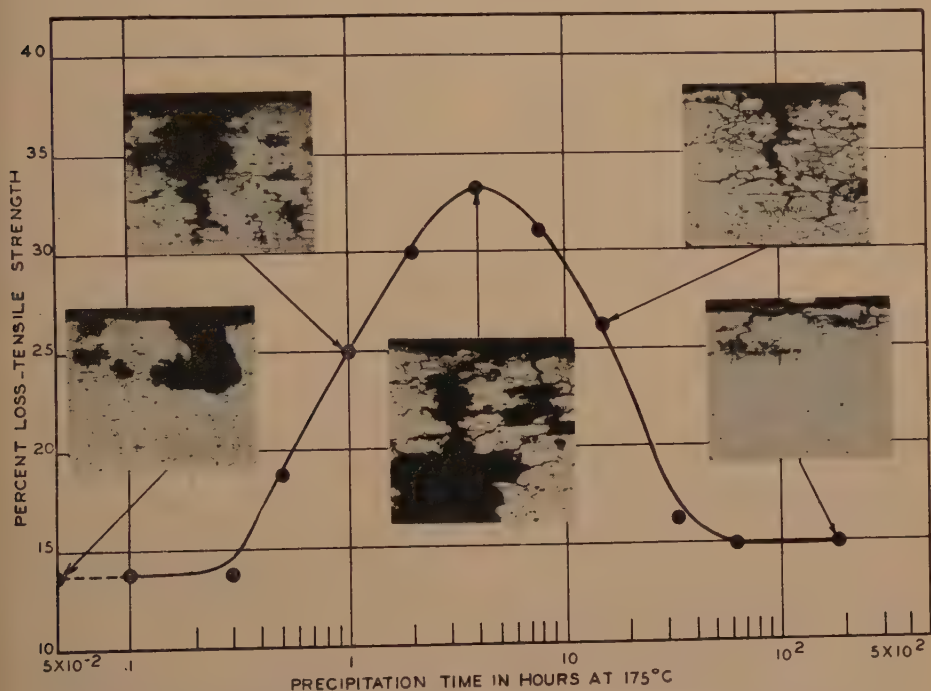


FIG. 8.—CHANGE IN CHARACTER AND INTENSITY OF CORROSIVE ATTACK OF 24S-T AFTER PRECIPITATION TREATMENT AT 175°C.

Micrographs are cross sections. Original magnification 250; reduced $\frac{1}{2}$ in reproduction Keller's etch.

the corrosion resistance remains equal to that characteristic of the room-temperature aged condition; a second in which the corrosion rapidly rises to a maximum and falls again to approximately its initial value; and a third during which the degree of corrosion remains constant and, approximately, equal to the initial value. The micrographs show that there is not a complete return to the initial conditions, in that intercrystalline corrosion is still evident; and the fact that the ultimate corrosion resistance is, on the average, slightly lower than its initial value, further substantiates the evidence of the micrographs. But the fact that the corrosion resistance

referred to again in the discussion of the mechanism.

DISCUSSION OF EXPERIMENTAL RESULTS

It is apparent from Fig. 7 that the postulated expression adequately represents the experimental data, since the five or six points fall on straight lines over a comparatively wide range of precipitation temperature and time. But, in addition to the maxima, the initial change in mechanical properties and initial, maximum, and ultimate susceptibility to intercrystalline corrosion can be similarly expressed. In fact, any corresponding point on the various property curves can be so

expressed, but the difficulty of choosing corresponding points, other than those of inflection, is apparent.

Thus, the important characteristics of the six sets of curves can be expressed in the same terms. Some data obviously are sacrificed to the simplification but the utility of the data is considerably increased and, after preliminary estimation of the time and temperature that yield a suitable combination of properties, the original curves may be consulted or additional experimental work performed. If more work is necessary, the field of possibilities will have been narrowed and the work correspondingly reduced.

For example, in commercial practice, the duration of the precipitation heat-treatment is limited by the economical use of furnaces and by the temperature control required for treatments at the higher temperatures. If 8 hr. is an economical time, reference to Fig. 7 shows at once that a temperature of $185^{\circ}\text{C}.$ will be required to attain maximum tensile strength and that the yield strength will be just below the maximum with the elongation reduced to about 25 per cent of its initial value, hardness at a maximum, and corrosion resistance reduced about 40 per cent of the possible reduction due to susceptibility to intercrystalline corrosion. By such trials, the optimum time and temperature can be chosen to meet the desired requirements for each property, as nearly as possible. For this purpose, interpolation and limited extrapolation is of considerable value and the single diagram affords a convenient summary of the mass of data otherwise presented.

It is also possible to determine the period of time at temperature before the various properties begin to change, particularly the susceptibility to intercrystalline corrosion. Thus, if the application requires exposure of the alloy to high temperatures, the line showing initial susceptibility will be important. In this

connection it should be emphasized that the region bounded by the two extreme lines defines structural conditions that provide a local potential difference in a suitable electrolyte; but, in other media, the corrosion does not necessarily develop because the potential is dependent on the nature and concentration of the electrolyte as well as on the metallurgical structure. Furthermore, the limit of extrapolation to lower temperatures is evident in the initial susceptibility to intercrystalline corrosion. If this line were extrapolated to $25^{\circ}\text{C}.$ it would indicate that the alloy becomes spontaneously susceptible in about 100,000 hr. (11 yr.), a fact not heretofore reported and certainly questionable. However, unlimited extrapolation is not possible because, in such processes, a minimum of energy is required for the diffusion and aggregation of the appropriate atomic groups forming the precipitate and, in this case, the minimum energy evidently is not attained at room temperature. Also, apparently the lower limit is not far from $130^{\circ}\text{C}.$, for, while the corrosion curve is still well defined, the curve of tensile strength (Fig. 1) does not show the marked inflections of those at higher temperatures, and a tensile-strength curve of material treated at $100^{\circ}\text{C}.$ did not show any of the characteristic inflections. Furthermore, the points of initial tensile strength, yield strength and hardness do not fall on the straight lines of Fig. 7 as defined by the five points obtained at higher temperatures, which seems to indicate a sharply decreasing initial sensitivity to the thermal treatment as measured by these property changes.

From Figs. 6 and 7 it will be observed that the maximum tensile strength is attained before maximum yield strength at each of the precipitation temperatures employed, but it should be noted also that the attainment of a simultaneous maximum is a function of the temperature, and a comparison of the slopes of the two

lines of maximum tensile strength and yield strength indicates that a simultaneous maximum is reached at 210°C. and 2 hr. Therefore, it appears that there is an advantage in the precipitation treatments at higher temperatures provided the more critical time and temperature can be controlled.

In addition, diagrams like Fig. 7 may be useful in defining the effect of various factors on the hardening characteristics and corrosion resistance. For example, the effect of cold-working between solution treatment and precipitation treatment could be readily appraised by the two parameters m and K . Furthermore, a convenient summary of the characteristics of different alloys could be made in the form of a table of parameters or with the corresponding diagrams, which could then be used to determine the alloy and appropriate properties and corrosion resistance. In this connection, it should be noted that after verification of the relationship it would not be necessary to employ six sets of isothermal curves.

With regard to the mechanism of age-hardening and its relationship to corrosion phenomena, the close coincidence of the increase in hardness with the maximum susceptibility to intercrystalline corrosion should be observed (Fig. 7). The point of increasing hardness corresponds to the third stage of age-hardening characterized by Cohen as the beginning of general precipitation. At this point, the degree of intercrystalline corrosion begins to decrease (as measured by decreasing loss in tensile strength) until it becomes negligible as a factor in lowering the corrosion resistance, which returns to that characteristic of the material in its room-temperature aged condition. The disappearance of effective intercrystalline corrosion is in conformity with the progressive elimination of the source of the local potential difference, presumably by the general precipitation within the grains.

Likewise, the initial susceptibility to intercrystalline corrosion and the eventual return to the initial corrosion resistance may be correlated, respectively, with the beginning of grain-boundary precipitation and the completion of general precipitation. The second hardness increase, shown by Cohen³ and related to grain-boundary precipitation, does not appear on the hardness curves, because, in the present work, the alloy was fully aged at room temperature before precipitation at the elevated temperature, a procedure different from that used to study the hardening mechanism.

The statement regarding the beginning of precipitation and eventual completion of the reaction should be interpreted only in terms of corrosion phenomena. The absolute significance of these points, with regard to structural changes, is unknown because the relationship in time between the appearance of a precipitate (not necessarily visual appearance) and the corresponding potential difference, together with its associated corrosion phenomena, has not been worked out. This is further emphasized by the fact that the microstructure shows evidence of intercrystalline attack when the degree of corrosion, as measured by loss in tensile strength, has returned to that characteristic of a pitting form of attack. Thus, while this latter point is of practical significance, it should not be interpreted in absolute terms; apparently it signifies a reduction of potential to a point where the resultant corrosion is approximately equivalent to that caused by the local heterogeneity in room-temperature aged material. A possible explanation is that the initial grain-boundary precipitation depletes the matrix to an extent that, after general precipitation, there still remains a small concentration difference between the grains and their boundaries, which results in a potential difference. This hypothesis would explain the fact that intercrystalline

corrosion persists; and the fact that the corrosion finally reaches a *constant* low value indicates that the precipitation reaction is complete.

The evidence presented that both the mechanical properties and susceptibility to intercrystalline corrosion can be expressed in the same terms, and that there is correspondence at the point of generalized precipitation with an accepted mechanism of age-hardening, appears to indicate that corrosion phenomena may be brought into the general picture of the age-hardening mechanism. Therefore, controlling factors will be common to both aspects of age-hardening alloys, and the relationship between the various properties is fixed and determined by the functional form of the expression connecting precipitation with the properties. For example, the relationship between maximum tensile strength and corrosion resistance means that both cannot occur together, since, apparently, a certain degree of precipitation is required for the former which lowers the latter, and this state persists throughout the range of time and temperature investigated.

In connection with the hardening mechanism, it is of interest to note that the apparent energy of diffusion, Table 1, is of the same order of magnitude as that found by Brick and Phillips⁷ for copper and magnesium in aluminum; namely, 31,400 and 29,000 cal., respectively. It should be understood, however, that little significance is attached to these values beyond the fact that they appear to add additional indirect evidence of the general unity of mechanism governing corrosion phenomena and mechanical properties insofar as diffusion is the common factor, which makes it possible to express both in the same terms.

SUMMARY

1. It is shown that the effect of precipitation time and temperature on both

the initial change and ultimate maximum mechanical properties and initial, maximum and ultimate susceptibility to intercrystalline corrosion of 24S-type aluminum alloys can be expressed by an equation of the form:

$$t = K \cdot 10^{m/T}$$

Therefore, since these various properties can be represented by the same relationship; it is possible to plot them on the same coordinates (Fig. 7), which provides a convenient method of summarizing the large volume of data and thereby facilitates the choice of optimum precipitation time and temperature with regard to their simultaneous but unequal effect on the different properties.

2. It is further shown that the character and intensity of corrosion, as a function of precipitation time, may be correlated with the previously proposed mechanism of age-hardening whereby grain-boundary precipitation and general precipitation take place in stages. The appearance of grain-boundary precipitation results in intercrystalline corrosion, which increases to a maximum at the time when general precipitation begins, after which the degree of corrosion decreases until it attains a constant low value indicating that the reaction of general precipitation is complete.

3. The simultaneous occurrence of maximum tensile strength and maximum yield strength is dependent on precipitation temperature and both attain a simultaneous maxima after treatment for 2 hr. at 210°C.

4. Because initial changes in properties may be expressed by the equation given above, it is possible to define the time and temperature permissible in high-temperature applications, especially with regard to the initial susceptibility to intercrystalline corrosion.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to the members of the staff of

Aluminium Laboratories Limited for their cooperation, and particularly to Miss K. Davy, who carried out the large number of tests and treatments involved.

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DISCUSSION

(A. H. Geisler presiding)

A. H. GEISLER.*—In this very interesting paper the author has demonstrated a straight-line relationship between temperature and time for the various deflections in the aging curves. The slopes of the straight lines provided values in Table 1 which were referred to as "heats of diffusion." Perhaps the quantity would be more appropriately defined as "heat of precipitation," since the precipitation process is the one actually occurring, and this involves nucleation as well as diffusion. An additional process—that of re-solution at the elevated aging temperature of precipitated particles formed during the prior aging period at room temperature—is also operative and may have some influence on the measured heats of reaction. The prior presence of a precipitate formed at room temperature would probably be more influential at the lower aging temperatures and possibly explains the divergence from the straight line of some of the data for aging at 130°C.

W. D. ROBERTSON (author's reply).—It is certainly true that the quantity that I have designated "apparent heat of diffusion" is a complex quantity involving more than the activation energy of diffusion. For this reason it was stated that little significance should be attached to these values beyond the fact that

they appear to support the general mechanism through which the various properties may be correlated.

With regard to the departure of the low-temperature points from the straight line, it is possible that the presence of the prior precipitate affects the rate of reaction. But, it could also be explained by the fact that a minimum energy of activation is required for the process of diffusion and nucleation. The fact that the curves obtained at 130° are relatively flat and that no maxima were obtained at 100° up to 2 hr. seemed to indicate that the limiting required energy input had been reached below which no appreciable reaction could take place.

E. H. DIX.*—I should like to congratulate Mr. Robertson on his excellent handling of the data and on his presentation.

I have not had an opportunity to read the paper in detail, so I wonder if Mr. Robertson stressed the marked effect of cold-work prior to artificial aging on the response of the alloy to artificial aging. This is recognized in specifications in this country, so that there are at least four different tempers of artificially aged 24S.

Coiled strip that has practically no effective cold-work in it, or material that is re-heat-treated by a customer and is not subsequently cold-worked when artificially aged becomes what we call T80 temper. On the other hand, commercial flat sheet, which receives some cold-working and flattening responds more effectively to the aging, and when artificially aged, becomes T81.

Some of the aircraft manufacturers have stretched shapes formed from sheet about 4 per cent, and that product when artificially aged becomes T84. Then there is a grade of sheet that is given about 5 per cent cold-work after heat-treatment, and when that is artificially aged it becomes T86. The strength of the artificially aged tempers are progressively higher in the order discussed.

I mention these various tempers because I assume that the data here are on material that has no cold-work. Is that right?

W. D. ROBERTSON.—Yes.

* Aluminum Company of America, New Kensington, Pennsylvania.

* Aluminum Co. of America, New Kensington, Pennsylvania.

E. H. DIX.—I think that is an important point to keep in mind.

W. D. ROBERTSON.—The variable of cold-working was not included in this investigation. However, I think that its effect would be to shift the straight lines in the direction of shorter times. This would be in conformity with the fact that diffusion is more rapid in cold-worked material than in material that is in the as-quenched condition.

T. C. WILSON.*—Have these aging temperatures been extended to temperatures higher than those shown on the graphs?

W. D. ROBERTSON.—No.

T. C. WILSON.—The point I want to bring out is that these straight lines go into hooks with a number of these diffusion reactions, as the temperatures are raised, and approach some limiting higher temperature. In your case, that limiting temperature would be the temperature at which the specimens were solution-heat-treated, I think. Just what the temperature is where the straight line starts to curve back is fairly important in order to define the slope of the straight-line portion.

This hooklike shape, followed by a straight line, appears, for example, in the transformation of austenite to pearlite when the times for a given percentage of transformation are

plotted against the reciprocal of the absolute temperature.

W. D. ROBERTSON.—I did not anticipate the turning of the straight lines. In fact, I am not sure that the austenite-pearlite transformation is exactly analogous with the precipitation of CuAl_2 from solid solution.

T. C. WILSON.—Analogous in that they are both diffusion reactions in the solid state.

W. D. ROBERTSON.—Yes.

T. C. WILSON.—I think you would find that it would hook around.

W. D. ROBERTSON.—My reason for not going to higher precipitation temperatures is that the reaction proceeds at such a rate that it cannot be accurately controlled. For example, the shortest precipitation time employed at 205° was $1\frac{1}{2}$ minutes.

(Written discussion).—Further consideration of Mr. Wilson's point regarding the turning of the straight lines shows it is theoretically possible. Thus, the phase diagram shows that as the precipitation temperature is raised the concentration gradient of diffusion is decreased and consequently the rate of diffusion also. In practice, however, the reaction proceeds so rapidly at the lower temperatures that extremely short times would be required to obtain experimental verification, and from the work already done it appears doubtful whether such data could be obtained.

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Diffusion in R301 Alloy and Its Effect on the Corrosion Resistance

By L. F. MONDOLFO,* MEMBER A.I.M.E.

(New York Meeting, October 1945)

R301 is a clad aluminum alloy, composed of a core of a duralumin-type alloy clad with a magnesium silicide alloy. It differs from other well-known clad alloys in that the cladding and the core respond to the same heat-treatments, and therefore the cladding contributes appreciably to the mechanical properties of the material. In Table 1 are reported the compositions of the core and cladding alloy for the material used for the experiments.

TABLE 1.—*Chemical Composition of R301 Used for the Experiments*

Element	Core	Cladding
Cu.....	4.45	0.01
Fe.....	0.57	0.42
Si.....	0.98	0.71
Mg.....	0.41	0.99
Mn.....	0.78	0.54

In clad aluminum alloys where the core contains copper and the cladding does not, at elevated temperatures the copper tends to diffuse from the core through the cladding. This fact is well known and many investigations have been conducted to determine the features of this diffusion.¹⁻⁷ Most of those investigations cover materials clad with pure aluminum; the present investigation covers a material clad with an alloy. Since the cladding thickness on R301 varies with the gauge, as shown in Table 2, several gauges were investigated.

Manuscript received at the office of the Institute May 7, 1945. Issued as T.P. 1940 in METALS TECHNOLOGY, December 1945.

* Research Metallurgist, Reynolds Metals Co., Glendale, New York.

¹ References are at the end of the paper.

TABLE 2.—*Nominal Thickness of Cladding on R301*

Gauge	Thickness of Cladding on Each Face, Per Cent
0.024 or less.....	10
0.025 to 0.039.....	7.5
0.040 to 0.101.....	5
0.102 or heavier.....	2.5

MATERIAL AND PROCEDURE

The material used was sheet of the following gauges: 0.025, 0.040, 0.064, 0.102, 0.170. Cut in pieces approximately 3 by 5 in., it was in the cold-rolled state and was soaked for increasing times at the following temperatures: 910°F., 940°F., 970°F.

A Lindberg cyclone furnace was used for the experiments. The procedure was as follows: The furnace was started empty with controlling pyrometer set at the determined temperature. After the furnace had reached that temperature, it was run for some 20 to 30 min. empty, in order to allow the temperature inside to become stabilized. Then the first samples were introduced. A load thermocouple, with recording pyrometer, was connected with the sample of the heaviest gauge. About 10 min. was required for the material to reach temperature and the soaking time was counted from that point.

After 200 min. soaking, the second group of samples was introduced without stopping the furnace. After 200 min. more, the third group of samples was introduced, and so on, until the last sample had been introduced. Every time the furnace was opened and new samples were added, a drop of temperature was registered by the thermocouple connected with the material

TABLE 3.—Results of Tests

Sample No.	Nominal Time, Min.	910°F.						940°F.						970°F.					
		Actual Time, Min.	Percent-age of Cu		Diffusion in 10 ⁻⁴ In.		Type of Corrosion ^b	Actual Time, Min.	Percent-age of Cu		Diffusion in 10 ⁻⁴ In.		Type of Corrosion	Actual Time, Min.	Percent-age of Cu		Diffusion in 10 ⁻⁴ In.		Type of Corrosion
			Spectro-graphic	Potential	A ^a	B			Spectro-graphic	Potential	A	B			Spectro-graphic	Potential	A	B	
0.025 GAUGE																			
1	CR	CR	0.01	0.01	13	68	P	CR	0.01	0.01	13	68	P	CR	0.01	0.01	13	68	P
2	0	4	0.01	0.01	32	100	P	2	0.01	0.01	41	99	P	2	0.09	0.06	67	127	P
3	10	15	0.10	0.08	59	141	P	3	18	0.55	0.26	99	179	P	15	0.25	0.34	165	187
4	20	25	0.14	0.14	76	175	P	4	30	0.69	0.33	158	187	P	25	0.74	0.60	187	Tr
5	30	35	0.32	0.20	95	187	P	5	32	0.48	0.37	187		P	35	0.74	0.79		Tr
6	40	50	0.24		129		P	6	35	0.48	0.44			P	45	0.87	0.98		Tr
7	60	65	0.60	0.40	170		P	7	60	0.75	0.70			Tr	55		1.25		Tr
8	80	87	0.75	0.50	187		P	8	63	0.72	0.77			Tr	85	1.85	1.86		Tr
9	100	110	0.90	0.53			P	9	105	0.84	1.20								Tr
10	150	160	1.14	1.04			P	10	175	2.02	1.78								Tr
11	200	195	1.32	1.38			P	11	180	1.75	2.02				135	2.13	2.55		Tr
12	250	260	1.54	1.66			P	12	260	1.80	2.28				200	1.63	2.88		Tr
13	300	307	1.72	2.15			P	13	305	1.88	2.45				290	3.20	2.93		Tr
14	400	413	1.80	2.15			P	14	400	2.07	2.80				390	3.73	3.04		Tr
15	600	610	1.97	2.76			P	15	600	2.13	2.66				605	2.98	3.44		Tr
16	800	805	2.90	2.95			P	16	800	2.10	2.95				825	2.80	3.50		Tr
17	1,000	1,010	2.80	2.95			P	17	1,000	2.85	3.15				1,015	4.30	3.40		Tr
18	1,200	1,200	3.00	3.00			P	18	1,190	3.30	3.30				1,200	4.50	3.64		Tr
0.040 GAUGE																			
1	CR	CR	0.01	0.01	10	50	P	CR	0.01	0.01	10	50	P	CR	0.01	0.01	10	50	P
2	0	4	0.02	0.01	40	113	P	2	2	0.02	0.01	47	108	P	2	0.05	0.02	68	122
3	10	15	0.07	0.01	68	142	P	3	18	0.04	0.01	117	170	P	15	0.09	0.36	172	200
4	20	25	0.12	0.05	90	156	P	4	30	0.29	0.23	140	200	P	25	0.52	0.66	200	Tr
5	30	35	0.25	0.08	97	170	P	5	32	0.45	0.27	150		P	35	0.83	1.02		Tr
6	40	50	0.15		120	180	P	6	35	0.47	0.30	155		P	45	0.82			Tr
7	60	65			140	195	P	7	60	0.57	0.55	200		P	55	1.02	1.60		Tr
8	80	87	0.65	0.28	170	200	P	8	63	0.70				P	85	2.05	2.37		Tr
9	100	110	0.80	0.36	198		P	9	105	0.80	1.17			P					Tr
10	150	160	0.80	0.70	200		Tr	10	175	1.23	1.76								Tr
11	200	195	1.12	0.93			Tr	11	180	1.23	1.87				135	1.04	3.07		Tr
12	250	260	1.14	1.20			P	12	260	1.75	2.14				200	3.38	3.50		Tr
13	300	307	1.68	1.40			P	13	305	1.84	2.61				290	3.70	4.00		Tr
14	400	413	1.88	1.99			P	14	400	2.07	2.91				390		4.00		Tr
15	600	610	1.92	2.28			P	15	600	2.13	3.17				605	4.00	4.00		Tr
16	800	805	1.85	2.41			P	16	800	2.23	3.40				825	4.09	4.00		Tr
17	1,000	1,010	2.70	2.52			P	17	1,000	3.20	3.38				1,015	4.30	4.00		Tr
18	1,200	1,200	2.95	2.67			P	18	1,190	3.52	3.40				1,200	4.50	4.00		Tr
0.064 GAUGE																			
1	CR	CR	0.02	0.02	5	35	P	CR	0.02	0.02	5	35	P	CR	0.02	0.02	5	35	P
2	0	4	0.02	0.02	14	53	P	2	2	0.02	0.02	15	55	P	2	0.05	0.02	30	80
3	10	15	0.02	0.02	30	95	P	3	18	0.02	0.02	60	145	P	15	0.04	0.06	100	180
4	20	25	0.03	0.02	45	120	P	4	30	0.03	0.06	87	185	P	25	0.08	0.10	135	220
5	30	35	0.03	0.02	54	140	P	5	32	0.03	0.07	90	190	P	35	0.06	0.16	155	270
6	40	50	0.05	0.05	74	170	P	6	35	0.04	0.08	95	195	P	45	0.03	0.18	195	300
7	60	65	0.05	0.08	88	205	P	7	60	0.17	0.14	140	205	P	55	0.12	0.22	215	320
8	80	87	0.05	0.11	105	245	P	8	63	0.16	0.15	145	270	P	85	0.47	0.42	310	Tr
9	100	110	0.16	0.16	130	280	P	9	105	0.46	0.28	205	320	P					Tr
10	150	160	0.17	0.26	180	320	P	10	175	0.63	0.62			P	135		0.75		Tr
11	200	195	0.26	0.30	230		P	11	180	0.60	0.54			Tr	200	1.53	1.05		Tr
12	250	260	0.56	0.41	320		P	12	260	0.77	0.85				290	1.54	1.50		Tr
13	300	307	0.65	0.64			P	13	305	0.69	1.03				390	1.20	1.86		Tr
14	400	413	0.75	0.85			Tr	14	400	1.00	1.34				605	1.54	2.50		Tr
15	600	610	1.20	1.34			P	15	600	1.43	1.93				825	2.58	2.85		Tr
16	800	805	1.48	1.60			P	16	800	1.55	2.30								Tr
17	1,000	1,010	1.33	1.91			P	17	1,000	1.63	2.51				1,015	2.95	3.02		Tr
18	1,200	1,200	1.70	2.08			P	18	1,190	2.40	2.68				1,200	3.46	3.32		Tr

^a Values in columns A and B represent average thicknesses of zones of diffusion in zones A and B, in hundred thousandths of an inch.^b P, pitting; Tr, trace of intergranular; I, intergranular.

TABLE 3.—(Continued)

Sample No.	Nominal Time, Min.	910°F.						940°F.						970°F.									
		Actual Time, Min.		Percent- age of Cu	Diffusion in 10 ⁻² In.		Type of Corrosion ^b	Actual Time, Min.		Percent- age of Cu	Diffusion in 10 ⁻² In.		Type of Corrosion	Actual Time, Min. ^a		Percent- age of Cu	Diffusion in 10 ⁻² In.		Type of Corrosion				
		Spectro- graphic	Potential		A ^a	B		Spectro- graphic	Potential		A	B		Spectro- graphic	Potential		A	B					
0.102 GAUGE																							
1	CR	CR	0.01	0.01	6	38	P	CR	0.01	0.01	6	38	P	CR	0.01	0.01	6	38	P				
2	0	4	0.01	0.01	12	45	P	2	0.01	0.01	13	45	P	2	0.01	0.01	25	60	P				
3	10	15	0.01	0.01	27	85	P	18	0.01	0.02	60	135	P	15	0.01	0.08	95	155	P				
4	20	25	0.01	0.01	39	109	P	30	0.01	0.06	85	155	P	25	0.04	0.14	140	185	P				
5	30	35	0.01	0.01	47	130	P	32	0.07	0.07	88	160	P	35	0.09	0.17	165	225	P				
6	40	50	0.01	0.06	65	150	P	35	0.08	0.08	90	168	P	45	0.13	0.22	205	255	P				
7	60	65	0.01	0.07	80	167	P	60	0.15	0.15	133	223	P	55	0.21	0.34	225		P				
8	80	87	0.05	0.11	95	215	P	63	0.18	0.18	140	227	P	85		0.60	255		Tr				
9	100	110	0.09	0.15	111	231	P	105	0.36	0.35	195	255	P						Tr				
10	150	160	0.41	0.24	150	255	P	175	0.63	0.55	255		P						Tr				
11	200	195	0.41	0.34	185		P	180	0.75	0.65			Tr	135	1.43	0.95			Tr				
12	250	260	0.57	0.43	255		P	260	0.84	0.78				200	1.75	1.40			I				
13	300	307	1.24	0.60			P	305	0.77	1.12			I	290	1.60	1.72			I				
14	400	413	1.32	0.81			Tr	400	1.20	1.33			I	390	2.05	2.21			I				
15	600	610	1.45	1.06			I	600	1.50	1.80			I	605	3.10	2.65			I				
16	800	805	1.70	1.42			I	800	1.83	2.10			I	825	3.30				I				
17	1,000	1,010	1.70	1.62			I	1,000	1.95	2.46			I	1,015	3.55	3.30			I				
18	1,200	1,200	1.75	1.84			I	1,190	3.00	2.80			I	1,200	2.95				I				
0.170 GAUGE																							
1	CR	CR	0.01	0.01	3	15	P	CR	0.01	0.01	3	15	P	CR	0.01	0.01	3	15	P				
2	0	4	0.01	0.01	32	65	P	2	0.01	0.01	34	62	P	2	0.01	0.01	45	80	P				
3	10	15	0.01	0.01	65	110	P	18	0.01	0.01	90	135	P	15	0.01	0.01	105	170	P				
4	20	25	0.01	0.01	78	140	P	30	0.01	0.01	115	175	P	25	0.01	0.01	130	210	P				
5	30	35	0.01	0.01	90	150	P	32	0.01	0.01	120	180	P	35	0.01	0.01	150	230	P				
6	40	50	0.01	0.01	110	170	P	35	0.01	0.01	125	190	P	45	0.01	0.01	165	250	P				
7	60	65	0.01	0.01	120	190	P	60	0.01	0.01	155	240	P	55	0.01	0.01	180	280	P				
8	80	87	0.01	0.01	135	215	P	63	0.01	0.01	160	245	P	85	0.01	0.08	220	330	P				
9	100	110	0.01	0.01	155	240	P	105	0.01	0.01	195	290	P						P				
10	150	160	0.01	0.01	175	275	P	175	0.10	0.10	245	330	P						P				
11	200	195	0.01	0.01	195	280	P	180	0.12	0.12	245	340	P	135	0.21	0.16	275	390	P				
12	250	260	0.01	0.08	220	325	P	260	0.55	0.20	295	410	P	200	0.13	0.28	350	425	P				
13	300	307	0.02	0.10	240	350	P	305	0.63	0.28	320	425	P	290	0.80	0.62	425		Tr				
14	400	413	0.03	0.18	295	400	P	400	0.71	0.42	420		Tr	390	1.18	0.80			I				
15	600	610	0.05	0.37	375	425	P	600	0.65	0.90	425		I	605	0.83	1.52			I				
16	800	805	0.22	0.65	425		Tr	800	0.70	1.03			I	825	3.06	2.15			I				
17	1,000	1,010	0.48	0.82			I	1,000	0.97	1.65			I	1,015	3.00	2.68			I				
18	1,200	1,200	0.70	1.02			I	1,190	1.50	1.96			I	1,200	3.52	2.95			I				

first introduced. At the beginning, when the load in the furnace was small, this drop of temperature was around 30°F., and it decreased proportionally with every addition of samples. When the last samples were introduced (at which time the load in the furnace was fairly large), the drop in temperature was not more than 10° to 15°F. at each introduction of samples. The time to bring back the load to the determined temperature decreased proportionally. About 9 to 10 min. was required at the beginning; at the end of the soaking only 3 to 4 min. was required.

These drops of temperature were disregarded for the samples already in the furnace. For each group of samples the soaking time was counted from the moment the load had reached the soaking temperature. When the last sample had been introduced and the load couple had reached the soaking temperature, the whole load was extracted from the furnace and quickly quenched in cold water.

Alorco compound was introduced into the furnace at the beginning of each soaking period, to minimize high-temperature deterioration, but in spite of

FIG. 1.



FIG. 2.



FIG. 3.

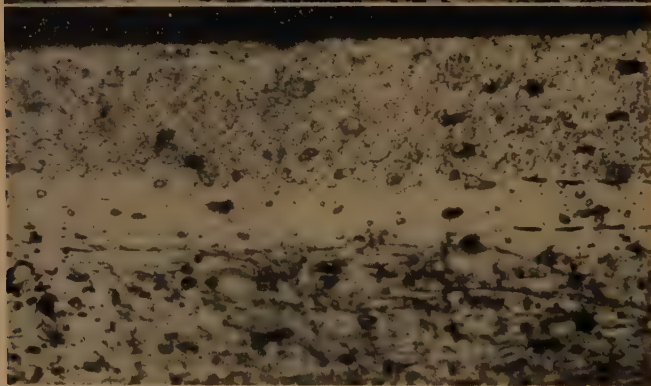


FIG. 1.—0.170-GAUGE MATERIAL. $\times 500$. ETCHED WITH SPECIAL ETCH.

The dotted lines show the boundaries of zones A and B of diffusion. Zone A from bonding line to farthest point of appearance of grain boundaries; zone B from bonding line to beginning of pitting in cladding.

FIG. 2.—0.025-GAUGE MATERIAL. $\times 500$. ETCHED 30 SECONDS WITH KELLER'S ETCH.

The two zones of diffusion are faintly visible.

FIG. 3.—0.025-GAUGE MATERIAL AS COLD-ROLLED. $\times 500$. ETCHED WITH SPECIAL ETCH.

The two zones of diffusion are clearly visible.

that some of the specimens, especially those soaked for long times at the higher temperatures, were somewhat blistered.

In Table 3 are reported the nominal soaking times and the actual soaking times as measured from the chart of the recording pyrometer.

After quenching, the samples were cut in three parts. One part was used for the spectrographic determination of the percentage of copper on the surface; one part was used for the microexamination of the diffusion; the third part was used for the electrolytic potential measurements and for the corrosion tests.

SPECTROGRAPHIC ANALYSIS

The samples for the spectrographic analyses were cleaned with grinding paper to remove the film of oxide formed during soaking, and then were analyzed by the spark method in a Dietert spectrograph. The spectrographic results (Table 3) are somewhat inconsistent, but their inaccuracy was expected in view of two main factors:

1. The spark used for spectrographic analyses will burn out a small amount of material, so that the analysis will not represent exactly the surface but will be the average of the material comprised between the surface and a point a few ten thousandths of an inch below the surface. No matter how closely the operations are controlled, the depth affected will vary from specimen to specimen, so that discrepancies will occur between the spectrographic determination and determinations made by other methods.

2. Different lines must be used for the densitometric determination of the percentage of copper present, and a perfect correlation between lines is not possible.

For these reasons the results of the spectrographic analyses were used only as a rough control of the other results and were not plotted in the curves of Figs. 4 to 8.

MICROEXAMINATION

The samples for metallographic examination were mounted in Bakelite, polished in the usual manner through grinding papers, alundum wheel and magnesia. A special etching method was used to bring out the effect of diffusion, consisting of etching by swabbing for one minute in a 3 per cent HF solution, followed by rinsing in hot water and immersion without drying in Keller's etch for 15 sec. This method of etching has the advantage over the normal Keller's etch of revealing very sharply two different zones of diffusion, whereas the Keller's reagent will reveal them only faintly. Fig. 1 shows a specimen etched by this method, in which lines have been drawn to show the approximate boundaries of these two zones. Fig. 2 shows a specimen etched with Keller's etch in which the two zones of diffusion are faintly visible. Fig. 3 shows cold-rolled specimen in which the special etch has revealed the two zones very clearly. In Table 3 the average thickness of these two zones are reported under A and B. Each value in the table represents the average of from four to six measurements, as determined in etched specimens at magnifications of 500. These values were obtained by measuring the distances from the surface to the outside boundaries of zones A and B, and then deducting these values from the nominal thickness of the cladding. In the left side of Figs. 8 to 12 these values have been plotted against the time on a logarithmic scale. On a whole the results of the microexamination are very consistent. Small discrepancies exist but they can easily be accounted for by the unavoidable local variations in thickness of the cladding, which are to be expected in run-of-the-mill material.

MEASUREMENT OF ELECTROLYTIC POTENTIAL

The samples for potential measurements, except some that were soaked a

FIG. 5.

FIG. 7.

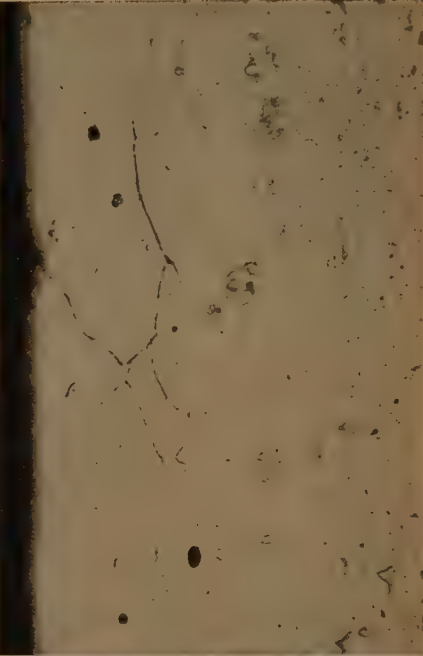


FIG. 4.

FIG. 6.

FIG. 4.—TYPICAL PITTING CORROSION. $\times 500$. ETCHED WITH KELLER'S ETCH.
FIG. 5.—BEGINNING OF INTERGRANULAR CORROSION, TERMED "TRACES OF INTERGRANULAR CORROSION." $\times 500$. NOT ETCHED.
FIG. 6.—TRACES OF INTERGRANULAR CORROSION. $\times 500$. NOT ETCHED.
FIG. 7.—INTERGRANULAR CORROSION. $\times 500$. NOT ETCHED.

long time at the higher temperatures, were prepared by abrading the surface with No. 0 paper just enough to remove the heavy oxide film formed during soaking. Some of the samples soaked at high temperature had a very heavy oxide film and abrading with No. 1F paper prior to the No. 0 was necessary. All the potential measurements were made with a saturated calomel electrode and a solution containing 57 grams NaCl and 10 c.c. concentrated H_2O_2 (30 per cent) per liter. The curve used for determining the percentage of copper in function of the potential was that determined by Brown and Coll.⁸ The results of the potential measurements, translated in percentage of copper at the surface, are reported in Table 3 and are plotted at the right side of Figs. 8 to 12. Discrepancies exist in the results of potential measurements but they are minor, and should not appreciably affect the value of the results.

CORROSION TESTS

The corrosion tests were conducted on the specimens that had been used for potential measurements. These specimens were aged 6 hr. at 350°F. and then corroded by immersion in a solution containing 57 grams NaCl and 10 c.c. of concentrated H_2O_2 (30 per cent) per liter. The time of immersion was 24 hr. After corrosion the specimens were cleaned in a 50 per cent solution of HNO_3 to remove the oxide and copper plated on the surface. The samples for microexamination were cut out of the most corroded part of each specimen, mounted in Bakelite, polished with the usual technique and examined at 100 and 500 diameters without etching.

The examination was limited to the determination of the type of corrosion present. The samples that had the shorter times of soaking showed only corrosion of the pitting type; those soaked for longer times showed corrosion of the intergranular type. The type of corrosion does not

change abruptly, but gradually. The samples that had intermediate soaking times showed corrosion of a type that was not decidedly either intergranular or pitting. This type of corrosion has been denominated "traces of intergranular," for lack of a better term. Fig. 4 shows the typical pitting type of corrosion; Figs. 5 and 6 show the limits within which the corrosion has been reported as "traces of intergranular." Fig. 7 shows corrosion decidedly of the intergranular type. The results of the corrosion tests are reported in Table 3 and plotted in Figs. 8 to 12. The following abbreviations have been used: P, to represent pitting corrosion; Tr, to represent traces of intergranular corrosion; I, to represent intergranular corrosion.

DISCUSSION OF RESULTS

Table 3 and Figs. 8 to 12 give a summary of the experimental results. In comparing the results of the metallographic determinations with the results of the potential measurements, the limits of the two zones of diffusion, A and B, become apparent. In Table 4 are reported the percentage of copper at the surface at the time that the boundaries of zones A and B reach the surface, as taken from

TABLE 4.—Percentage of Copper at the Surface When the Diffusion Lines Reach the Surface

Gauge	910°F.		940°F.		970°F.	
	A	B	A	B	A	B
0.025	0.41	0.19	0.41	0.20	0.42	0.19
0.040	0.40	0.21	0.41	0.23	0.43	0.19
0.064	0.40	0.19	0.42	0.19	0.39	0.20
0.102	0.43	0.20	0.41	0.21	0.42	0.21
0.170	0.41	0.21	0.40	0.20	0.39	0.20

Figs. 8 to 12. From Table 4 it is evident that the boundary of zone B represents the line dividing the zone in which the percentage of copper is approximately below 0.20 from the zone where the copper per-

centage is above 0.20, and the boundary of zone A divides the zone where the percentage of copper is approximately above 0.40 from the zone where it is below 0.40.

heat-treatment the solute is present in the matrix as particles with a well-defined identity. When the material is drastically etched with hydrofluoric acid, as in the method

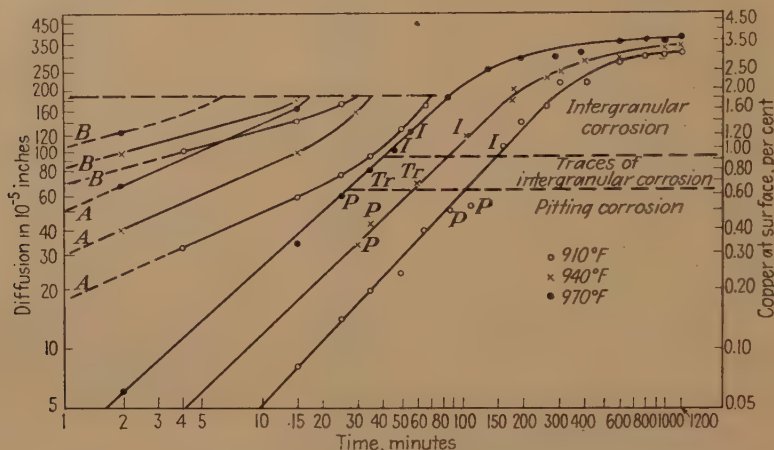


FIG. 8.—0.025-GAUGE MATERIAL.

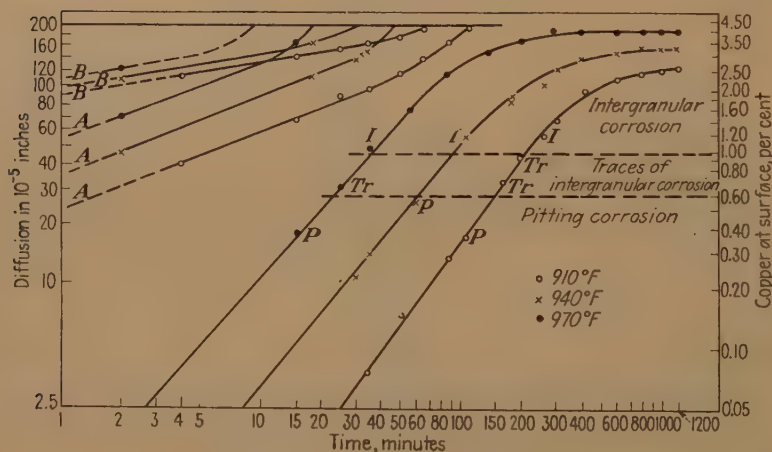


FIG. 9.—0.040-GAUGE MATERIAL.

To explain the significance of these zones, the constitution of the alloys must be taken into consideration. The cladding contains approximately 1 per cent Mg and 0.7 per cent Si, which, in material not containing copper, are present in the forms of Mg_2Si and Si. In the cladding both are in solid solution in the aluminum. When the material is allowed to age, precipitation starts, and a short time after

just described, the particles of magnesium silicide (and probably also of silicon) are attacked, and there results a pit whose size is many times greater than that of the particle that caused it. This accounts for the pitting clearly visible near the surface and for the general roughening of this zone, which, by reducing the reflectivity of the material, produces the darkened surface visible in Figs. 1 and 3.

The presence of copper that has diffused from the core in heat-treatment alters the structure of the material. When copper, magnesium and silicon are present in an

is the case for the cladding of R301. When the copper diffuses from the core, it combines with the magnesium silicide and silicon in solid solution, to form the

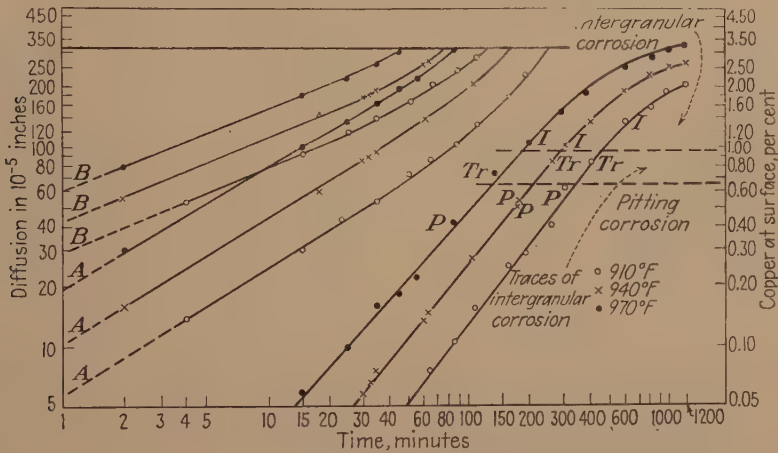


FIG. 10.—0.064-GAUGE MATERIAL.

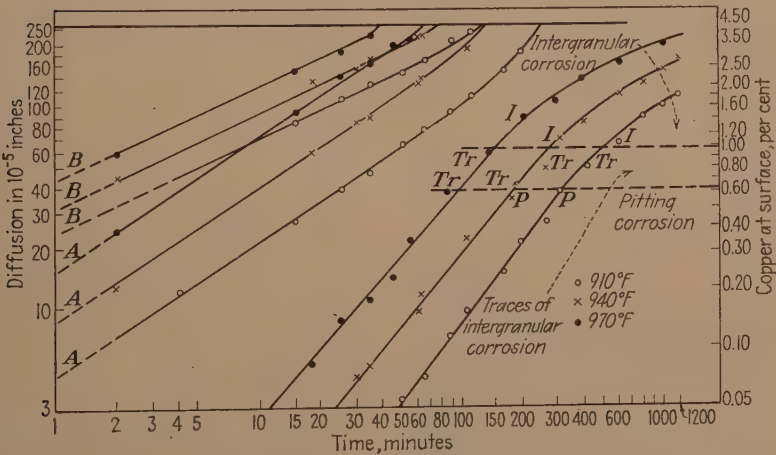


FIG. 11.—0.102-GAUGE MATERIAL.

aluminum alloy in certain proportions, a quaternary compound is formed,⁹⁻¹⁰ which has a composition approximately¹¹ Mg, 31.0 per cent; Cu, 15.0; Si, 28.0; Al, 26.0; which corresponds closely to the formula $\text{CuMg}_5\text{Si}_4\text{Al}_4$. This compound is formed only in alloys where the silicon content is above that required for the formation of magnesium silicide, which

quaternary constituent. This constituent, although stained by hydrofluoric acid, or etching reagents containing it is not attacked and eaten away as is the magnesium silicide. Therefore, when a large part of the silicide in the alloy is transformed into the quaternary compound, the pitting, which is produced by the action of the hydrofluoric acid on

the magnesium silicide is reduced to a very large extent and the etched surface under the microscope will appear almost white.

The second zone, which is delineated by

is also confirmed by the following observation: The boundary of zone B is a relatively straight line, as compared with the boundary of zone A, which has peaks

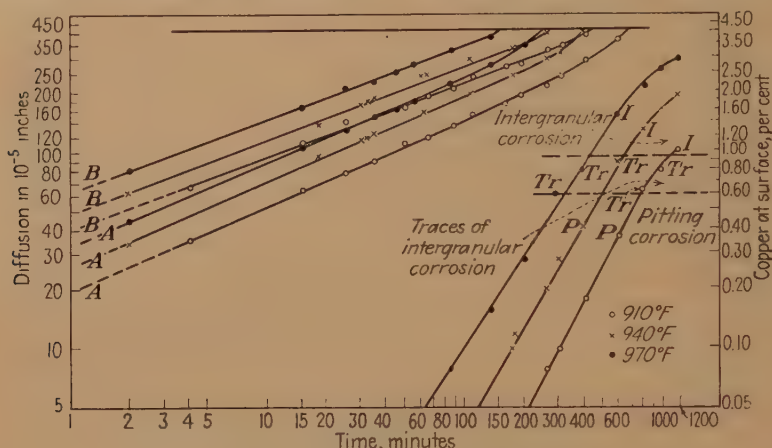


FIG. 12.—0.170-GAUGE MATERIAL.

the appearance of grain boundaries, begins to appear when the copper has reached about 0.40 per cent. Since the quaternary constituent contains approximately one half as much copper and silicon magnesium, the amount of copper that combines with magnesium and silicon in the cladding is approximately 0.30 to 0.35 per cent. Fig. 3 in Keller and Brown's paper¹² shows that with 0.10 per cent Cu the grain boundaries in Alclad 24S are clearly brought out by Keller's reagent. In a pure aluminum cladding all the copper is present as CuAl_2 . Since the grain boundaries in R301 are not revealed by Keller's etch before the percentage of copper in the cladding has reached 0.40 to 0.45, it is evident that in R301 the first copper to diffuse combines with magnesium and silicon to form the quaternary alloy, and only when all the available magnesium of silicon is combined will the copper form CuAl_2 . When the free copper (not combined with magnesium and silicon) has reached 0.05 to 0.10 per cent, there is sufficient CuAl_2 formed so that the etching will bring out the grain boundaries. This

in correspondence with the grain boundaries and valleys inside the grain. This would tend to indicate that the first copper to diffuse, as shown by the boundary of zone B, moves as a continuous front, and only when the copper is not fixed inside the grain in the form of a quaternary compound does the diffusion take place faster at the grain boundaries.

The diffusion of copper as a front, instead of in peaks and valleys as in claddings containing magnesium and silicon, has already been observed by Seeman and Dudek.⁶ The curves representing the diffusion of copper in the cladding, as measured by the 0.20 and 0.40 per cent Cu boundaries, are plotted in logarithmic scales in Figs. 4 to 8. These lines reveal that the first part of the curve, when plotted in logarithmic scale, is a straight line, as is to be expected from general considerations on diffusion. The last part of the diffusion curves, however, does not fall in a straight line, but shows an apparent acceleration of diffusion.

This is caused by the fact that when the copper has reached the surface it begins

to build up, changing the diffusion conditions. This effect, which is maximum in light-gauge material where the thickness of the cladding is less, and therefore the copper reaches the surface earlier, is present in all the materials examined. Although the experimental results are not accurate enough to detect exactly when the change from straight line to curve takes place, it is to be expected that as soon as the copper reaches the surface, a change in direction of the curve will take place, and become more and more pronounced, the higher the percentage of copper at the surface.

All the curves representing the percentage of copper at the surface have the same shape. The first part of the curve is a straight line, then there is a flattening down when complete diffusion is approached. The effect of the temperature is the same in all the curves—the higher the temperature, the steeper the curve. Several differences are to be noticed: The starting point is different for all the curves. Table 5 gives the time required by the copper to reach a concentration of 0.05 per cent at the surface. The time required for the copper to

TABLE 5.—*Time Required for the Copper to Reach 0.05 Per Cent at the Surface*

Gauge	Cladding Thickness, 10 ⁻⁶ In.	MINUTES		
		910°F.	940°F.	970°F.
0.025	187.5	10	4	18½
0.040	200	25	8	28½
0.064	320	48	27	13
0.102	255	47	23	11
0.170	425	210	120	62

reach the surface increases with the thickness of the cladding, as is to be expected. Material of 0.102 gauge, with a thickness of cladding lower than 0.064 material, shows copper at the surface earlier.

Another appreciable difference between the various gauges is the height reached by the curves. In 0.025 and 0.040 material the

saturation, as evidenced by a tendency of the diffusion curve to become parallel to the abscissa line, is reached within the time of the test, at least for the higher temperatures. In the heavier gauges, the diffusion not only begins later but also progresses at a much slower rate, so that within the time of the test not only is saturation not reached, but some of the curves (as, for instance, those for 0.170-gauge material) barely reach the point at which a decided deflection starts to show. This difference in behavior is produced evidently by the difference in thickness of the cladding, which, by increasing the distance the copper must diffuse to reach the surface, produces a lower gradient and therefore a slower diffusion.

The distance of the source of copper is not the only factor to influence the rate of diffusion. The amount of diffusion at the start has some influence. Table 6 shows the thickness of the zones A and B at the

TABLE 6.—*Thickness of Diffusion at the Start*

Gauge	Cladding Thickness, 10 ⁻⁶ In.	Number of Anneals in Fabrication	Thickness of Zones, 10 ⁻⁶ In.	
			A	B
0.025	187.5	3	13	68
0.040	200	2	10	50
0.064	320	1	5	35
0.102	255	1	6	38
0.170	425	0	3	15

start. The difference in the amount of diffusion in the cold-rolled material can be explained only if the previous history of the material is considered. The number of intermediate anneals in fabrication, shown in column 3, has a decided effect. The material undergoes the intermediate anneals in coil form and the time required to bring the coils up to the annealing temperature is of the order of 15 to 20 hr. This explains why, although the annealing temperature is well below 800°F., some diffusion takes place during annealing. The 0.025-gauge material, which has the

maximum amount of intermediate anneals, shows the highest amount of diffusion at the start. The 0.170-gauge material, which does not undergo any intermediate annealing, shows a very small amount of diffusion, which probably takes place during hot-rolling. There is a small difference in the amount of diffusion present in 0.064 and 0.102 gauge that cannot be due to the annealing, since both gauges underwent the same number of anneals. The reason for this may be that the 0.064-gauge material underwent a higher percentage of reduction after the last anneal than did the 0.102-gauge.

The results of the corrosion tests show that the type of corrosion is dependent only on the amount of copper that has diffused at the surface. The thickness of the cladding, the soaking time and temperature affect the corrosion only as a consequence of their effect on the percentage of copper at the surface. When the copper at the surface is below 0.60 per cent approximately, the corrosion is of the pitting type. When the copper at the surface is more than 0.60 per cent, the type of corrosion changes and traces of intergranular corrosion begin to appear. When the copper at the surface is above 0.90 per cent, the corrosion is decidedly intergranular.

CONCLUSIONS

1. Diffusion in R301 alloy follows the normal laws of diffusion. When plotted on a logarithmic scale, the diffusion at the beginning is a straight line. When the copper has reached the surface and cannot progress further, there is an apparent acceleration of the diffusion, which is caused by the building up of copper in the cladding. The rate of diffusion is dependent upon the temperature—the higher the temperature, the faster the diffusion. The rate of diffusion is also affected by the distance from the source of copper and by the amount of copper available, which is the amount in solid solution, rather than the total copper

present in the alloy. The fabricating practice has a decided effect on the amount of diffusion at the start and therefore affects also the subsequent diffusion to a certain extent.

2. Microexamination reveals two lines of diffusion, one corresponding to 0.20 per cent Cu and the other to 0.40 per cent Cu. The first line is the boundary between the zone where the magnesium and silicon in the cladding are in the form of Mg_2Si and Si and the zone where the magnesium and silicon have combined with diffused copper to form $AlCuMgSi$. The second line is the boundary between the zone in which all the diffused copper is combined with magnesium and silicon to form the quaternary $AlCuMgSi$ and the zone in which there is an excess of copper present in the form of $CuAl_2$. In the zone where the copper combines with magnesium and silicon, the diffusion takes place as a continuous front; in the zone where the copper forms $CuAl_2$, diffusion is faster at the grain boundaries.

3. The type of corrosion to which the material is susceptible in the aged state is directly dependent upon the percentage of copper at the surface. When the copper at the surface is below 0.60 per cent, the corrosion is of the pitting type; when it is above 0.90 per cent, the corrosion is of the intergranular type. Between these two percentages the type of corrosion changes gradually from pitting to intergranular. The thickness of the cladding, the soaking temperature and the soaking time affect the type of corrosion only as a consequence of their effect on the percentage of copper at the surface.

ACKNOWLEDGMENT

The author wishes to thank the Reynolds Metals Co. for the permission to publish this work; also, Messrs. T. L. Fritzlen and V. E. Flaherty, for their helpful suggestions, and Dr. W. E. Giles and Messrs. M. F. Rupp, R. S. Mapes, W. W. Hairston, L. E. Householder and H. B. Burrack

and their staffs for their collaboration in this investigation.

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DISCUSSION

(A. H. Geisler presiding)

A. H. GEISLER.*—Has the author investigated the influence of etching time upon the width of zones A and B? Does the width vary with etching time, and does the width of both zones vary, or of one zone in particular?

L. F. MONDOLFO. (author's reply)—There is no appreciable variation. I have investigated the etching several times. The result is that the pitted zone becomes more pitted, but the boundary does not move appreciably. At least, I was not able to measure any variation of the boundary. There may be slight variations, but they will be within the error of measuring.

* Aluminum Co. of America, New Kensington, Pennsylvania.

Superheating of Magnesium Alloys

BY N. TINER,* JUNIOR MEMBER A.I.M.E.

(Fall Meeting, October 1945)

THE mechanical properties of magnesium-alloy castings are greatly improved by grain refinement, and at present considerable attention is being paid to methods of obtaining fine-grained castings. One method of achieving this end is the use of proper melting and superheating techniques. These have been employed commercially to a great extent, but no comprehensive study of the subject appears to have been published at present. Numerous investigations found in the literature include some reference to superheating techniques,¹⁻⁴ and Achenbach, Nipper and Piwowarsky,⁵ based principally on thermal analysis, ascribe the grain-refining action of superheating to the influence of solid foreign particles or dissolved gases present in the melt upon the course of crystallization.

The primary purpose of this paper is to present the principal facts concerning the effect of superheating on grain size of magnesium alloys. Attempts are also made to explain the experimental results in terms of a general hypothesis. The investigations are limited chiefly to common commercial casting alloys.

In order to carry on this work, it was necessary to determine the factors influencing grain size and to develop a proper technique for the preparation of samples.

This paper represents part of a thesis submitted to the Graduate Committee of Stanford University, Calif., in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Manuscript received at the office of the Institute April 18, 1945. Issued as T.P. 1935 in METALS TECHNOLOGY, October 1945.

* Ankara, Turkey.

¹ References are at the end of the paper.

The preliminary tests made by the author indicated that the grain size of magnesium alloys resulting from the solidification of a melt is determined by alloy composition, presence of impurities, rate of cooling during solidification, thermal history of the melt and to some extent the structure of the charge used. The rate of cooling is in turn dependent upon the mass of the melt, pouring temperature, and dimensions, properties and temperature of the mold into which the melt is poured. The final grain size of the alloys is still further modified by heat-treatment subsequent to casting.

It is not within the scope of the present paper to discuss all of these factors, and it would suffice to note here that when equal amounts of magnesium alloys are prepared from the same alloying materials, melted in graphite crucibles under the same thermal conditions, then cast into graphite molds at a constant temperature, the resultant solids have the same grain size. By maintaining all other factors constant, it is thus possible to vary thermal conditions of a melt and to examine the grain size of resultant castings.

PRÉPARATION OF SAMPLES AND GRAIN-SIZE TESTING

The alloys investigated in this paper were taken from ingots made by Permanente Metals Corporation or prepared by the author with pure carbothermic magnesium and necessary alloying elements. Melting was carried out under a flux in a graphite crucible heated uniformly by an

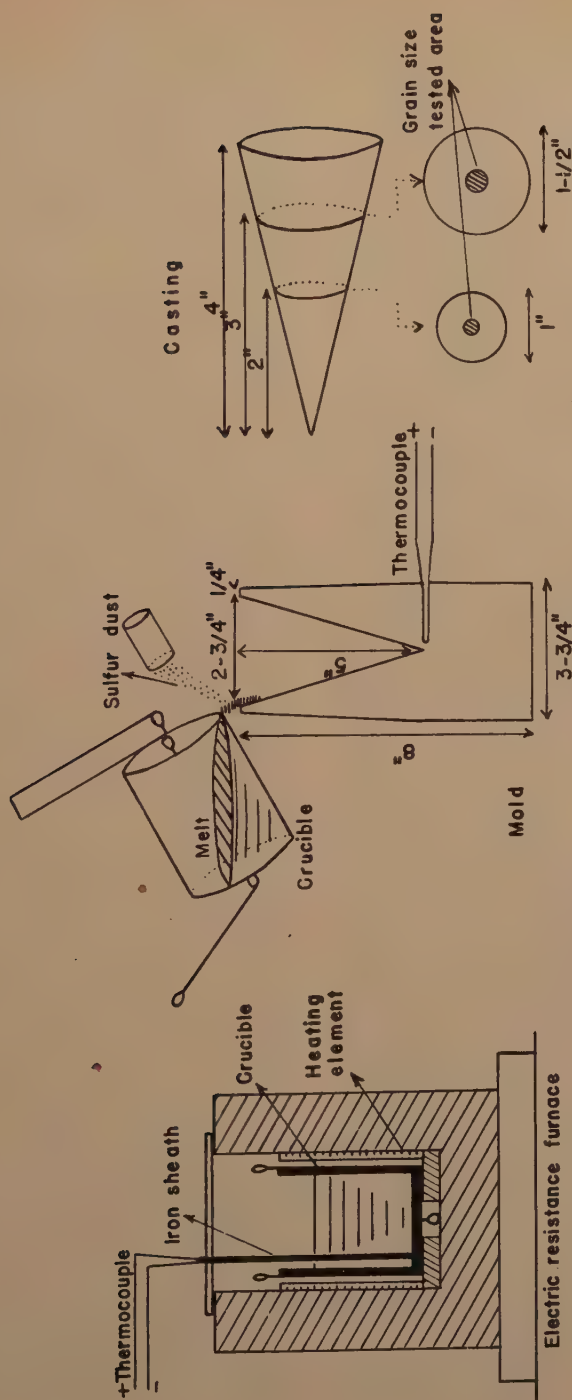


FIG. 1.—EXPERIMENTAL ARRANGEMENT FOR MELTING AND CASTING.

electric resistance furnace (Fig. 1). The flux consisted of 52.5 per cent KCl, 40 per cent MgCl_2 , 6 per cent BaCl_2 and 1.5 per cent CaF_2 . The crucible was 4 in. high, 3 in. in diameter, and was protected against heat by a metal-coated steel cylinder. The temperature was measured with a Chromel-Alumel thermocouple protected by an iron sheath and controlled within 5° to 10°C . by hand regulation of current input.

The molds were made of graphite and were of cone shape, 5 in. high and $2\frac{3}{4}$ in. in diameter at the base (Fig. 1). Graphite molds can be used many times, and eliminate the effect of sand condition on grain size. The cone shape makes castings easy to examine and gives information on the variation of grain size with the thickness of the sections, which is of technical importance. Two sections of the cones—the first 1 in. in diameter (referred to as small section), and the other $1\frac{1}{2}$ in. in diameter (referred to as large section)—were chosen as reference sections, and, to eliminate the effect of chilling, grain size was measured in the central region of the sections as shown in Fig. 1. The samples were prepared in duplicate, the sections were marked with a special device and cut carefully with a lathe, so that the error resulting from the change in thickness of the sections was negligible. The pouring and the mold temperatures were about 700° and 300°C ., respectively, as used in actual foundry practice.

The presence of large amounts of $\beta(\text{Mg-Al})$ phase in cast alloys makes the grain boundaries difficult to recognize. The samples, therefore, were subjected to proper solution heat-treatment for a systematic determination of grain size. They were heated in a salt-bath furnace for 16 hr. at 400° to 415°C ., then cooled in air. Heat-treatment may vary somewhat with the composition of the alloys. It should be noted however, that heating for a long time is to be avoided, since this

process may lead to some grain coarsening. The proper sections of the homogenized samples were roughly prepared and polished in the usual way. Etching was done with either glycol etchant or with a solution of 15 ml. of alcohol-saturated picric acid and 1 ml. of glacial acetic acid, the latter etchant being preferred for coarse-grained alloys.

Grain-size testing was done by the traverse method. The sample was placed upon a microscope stage, the stage was moved for about 3 to 4 mm. successively in two directions perpendicular to one another, the grains traversing the center of the cross hair of the eyepiece were counted, and the average number of grains per millimeter was determined. The average number of grains per square millimeter was found by multiplying the square of that number by a correction factor of 0.8. This factor was determined by a large number of experiments by counting the number of grains per square millimeter as in Jeffries' planimetric method⁶ and comparing the result with the number as determined above. The traverse method is rapid and gives more accurate results than the measurements made in actual laboratory practice by comparison with a special microscope grain-size eyepiece.

SUPERHEATING EXPERIMENTS

Effect of Superheating Temperature and Time

The experiments now to be described were intended to examine systematically the variation of grain size with superheating temperature and with time of holding the melts at that temperature. The alloy tested was carbothermic A.S.T.M. No. 17 alloy with 8.6 per cent aluminum, 2.0 zinc and 0.3 manganese.

The samples, weighing 180 to 200 grams, were melted in a graphite crucible under a melting flux. The temperature of the

melt was raised to the desired point and kept steady for different periods of time. At the end of each period, the crucible was taken from the furnace, cooled to 700°C. in still air, and immediately poured into graphite mold maintained at 300°C. The grain size at two reference sections of solid cones was determined as described above.

The results are shown in Table 1, which indicate that: (1) all other factors being

TABLE 1.—Average Grain Size of A.S.T.M. No. 17 Alloy Superheated to Various Temperatures for Different Periods

Super-heating Temperature, Deg. C.	Super-heating Time, Hr.	Grains per Sq. Mm.	
		Small Section	Large Section
700	½	40	32
700	3	25	18
750	½	35	30
750	3	75	72
800	½	50	40
800	3	98	75
850	0-½	285	270
850	½	280	250
850	3	292	265
900	½	240	224
980	½	95	80

practically constant, grain size decreases to a minimum value as the temperature of superheating is increased to 850° to 900°C. and at still higher temperatures there is a tendency for grain coarsening; (2) holding a molten alloy for several hours at temperatures of 750° to 800°C. produces some grain refinement; (3) as superheating temperature is raised to 850°C., or more, the time required for the grain refinement drops off to zero and a prolongation of superheating at these high temperatures has no additional effect; (4) thin sections have finer grains than thick ones; this was noticeable particularly for the sections with large differences in diameter.

It has been stated in the literature^{1,5} that a prolongation of superheating time is advantageous in producing finer grains. The foregoing results indicate this state-

ment to be true only when superheating is carried out at low temperatures.

Effect of Time of Cooling from Superheating to Casting Temperature

In the foregoing experiments, the melt was brought from superheating to casting temperature in a few minutes and immediately cast into molds. The present experiments were intended to investigate whether the time of holding the superheated melts at low temperatures before casting has any effect on grain size.

The alloys, weighing 180 to 200 grams, were melted in graphite crucible under a melting flux, heated to 850°C. for ½ hr., then cooled and held for different periods of time at the desired temperatures. At the end of each period, the crucible was taken from the furnace, cooled to 700°C. in still air, and immediately poured into graphite mold maintained at 300°C.

TABLE 2.—Average Grain Size of Alloys Held for Different Periods at Low Temperatures before Casting

Alloy Composition, Wt. Per Cent	Holding Temperature, deg. C.	Holding Time, Hr.	Grains per Sq. Mm.	
			Small Section	Large Section
8.6 Al-2.0 Zn-0.3 Mn.....	700	0	280	250
	700	½	25	18
	700	2	12	10
	750	2	75	62
	800	2	110	96
5.7 Al-2.9 Zn-0.33 Mn.....	700	0	120	95
	700	½	35	20
	700	1	22	15
	700	2	20	15

The grain-size measurements, shown in Table 2, indicate that the superheating effect on grain size is gradually and completely neutralized by holding the molten alloys for increasing periods at low temperatures before casting. The No. 17 alloy used in these and in the preceding experiments was taken from the same ingot. A comparison of the grain-size measurements suggests that when the molten alloy is held at a given temperature

for a sufficiently long period of time, the effect of previous melting conditions practically disappears. Within a certain limit, the castings have the same grain size whether the melt is brought to the desired temperature from lower or from higher temperatures.

Effect of Structure of Charge

These experiments deal with the effect of the structure of the charge upon the final grain size of magnesium alloys subjected to a given thermal treatment.

An alloy of A.S.T.M. No. 17, same composition as before, was melted in graphite crucible, and then cooled slowly in an enclosed atmosphere. The solid obtained had a coarse-grained structure, containing approximately 5 to 8 grains per sq. mm. Another sample of the same alloy was prepared by melting, superheating and casting into small chilled graphite molds. This casting had a fine-grained structure, containing 400 or more grains per square millimeter.

A 150-gram sample of the coarse-grained alloy was then quickly remelted in graphite crucible. When the temperature had reached 670°C., the crucible was taken from the furnace and the melt immediately poured into graphite mold maintained at 300°C. This procedure was repeated with a sample of the fine-grained alloy. The melt-

ing in both cases lasted about 5 min. Other samples were melted for $\frac{1}{2}$ hr. at 720°, 800° and 850°C., respectively, and cast at 700°C. into graphite mold.

Table 3 shows the average grain size of the castings prepared from coarse-grained and fine-grained alloys as described above. It is to be noted that: (1) all other factors being practically constant, the grain size of an alloy varies with the structure of the sample before melting; (2) this variation in grain size is pronounced when the melts are superheated at low temperatures, but decreases and practically disappears as the superheating temperature is increased.

Effect of Repeated Superheating

It has been found that the difference in the average grain size of the alloys obtained from coarse-grained and fine-grained charges practically disappears when the melt is superheated to high temperatures. The present experiments determine whether the average grain size remains constant when superheating the melts at high temperatures is repeated.

A melt of A.S.T.M. No. 4 alloy (5.7 per cent aluminum, 2.9 zinc and 0.33 manganese) was superheated to 840°C. in a graphite crucible for 15 min. The crucible was then taken from the furnace, cooled to 700°C., and the melt poured into three graphite molds maintained at 300°C. One cone was tested for grain size, the remaining two were remelted, superheated and cast under the same conditions as before. The procedure was repeated with the third cone. It was found that the three cones had 110, 98 and 105 grains per sq. mm. in small sections, and 90, 85 and 90 in large ones, respectively.

A melt of the alloy was superheated to 850°C. for 15 min. The crucible was then taken from the furnace, cooled to 700°C., one cone was poured and the crucible returned to the furnace to superheat the melt again to 850°C. for 15 min. Another cone was poured in the same manner, and

TABLE 3.—Average Grain Size of Castings Prepared from Coarse-grained and Fine-grained Alloys (A.S.T.M. No. 17)

Structure of Charge	Melting Time, Min.	Melting Temperature, Deg. C.	Grains per Sq. Mm.	
			Small Section	Large Section
Coarse.....	5	670	15	10
Fine.....	5	670	110	95
Coarse.....	30	720	20	15
Fine.....	30	720	66	40
Coarse.....	30	800	32	30
Fine.....	30	800	72	68
Coarse.....	30	850	280	270
Fine.....	30	850	285	262

the crucible returned to the furnace to superheat the melt to 850°C. for 15 min. before the third cone was poured. The procedure was carried out also with other alloys.

The results are given in Table 4. It can be noted that repeated superheating of molten magnesium alloys at high temperatures does not produce any appreciable change in the average grain size of the resultant castings.

TABLE 4.—Average Grain Size of Repeatedly Superheated Melts
GRAINS PER SQ. MM.

Alloy Com- position, Wt. Per Cent	First Superheat		Second Superheat		Third Superheat	
	Small Sec- tion	Large Sec- tion	Small Sec- tion	Large Sec- tion	Small Sec- tion	Large Sec- tion
5.7 Al-2.9 Zn- 0.33 Mn....	115	95	105	85	110	100
8.9 Al-2.0 Zn- 0.2 Mn....	160	125	150	120	145	115
9.0 Al-0.2 Mn.	150	110			140	105

It has been stated by Beck,¹ Achenbach, Nipper and Piwowsky⁵ that the effect of superheating carries over through remelting steps. The preceding experiments with charges of different grain size and with repeatedly superheated melts indicate this statement to be true to a limited extent; namely, when superheating is carried out at low temperatures. When the final superheating before casting is done at a proper temperature, no additional benefits are realized from previous superheating. The same result was reported recently in an article by Nelson.⁴

Effect of Stirring

It was found that superheating effects may be obtained at 800° to 750°C., but the effect at these temperatures was rather small and the time required long. It would naturally be of interest to investigate whether stirring the melts at low temperature of superheat has any effect on

grain size of castings. To this end, a sample of molten No. 17 alloy was strongly stirred for 30 min. with an electrically driven iron stirring rod. The temperature of the melt was maintained at about 800°C. To prevent an excessive heating of the electric stirrer, the stirring rod was made long and constantly cooled at one end with a wet cloth. Burning of the melt was partially overcome by continual addition of melting flux. When stirring was completed, the crucible was taken from the furnace, cooled to 700°C., and the melt was immediately poured into graphite mold. Grain-size testing showed that the castings had an average of 290 grains per sq. mm. in small section and 260 in large one. Stirring at 800°C. causes, then, a considerable grain refinement of the alloys.

The procedure described may be applied to actual foundry practice, to save some of the heat power used in superheating. It is necessary, however, to develop a proper stirring technique in order to prevent oxidation of the melt and introduction of flux into castings. It should also be noted that if stirring is carried out at 700° to 720°C., there is a tendency for grain coarsening.

Superheating in Vacuum

Superheating of magnesium alloys is carried out usually under a melting flux in the presence of air. It is desirable, therefore, to determine whether the atmospheric gases are associated with the alloy and have an influence on grain size of castings.

Magnesium alloys cannot easily be superheated in the common vacuum (or controlled-atmosphere) furnace for melting small metal samples by induction; because magnesium, owing to its high vapor pressure (2.28 mm. of mercury at 650°C. and 166 at 950°C.), evaporates and condenses in the cold parts of the furnace. For this reason a special technique was developed to superheat the melts under high vacuum.

Melting was done in small graphite crucibles, $1\frac{1}{4}$ in. high and $\frac{1}{2}$ in. in diameter. The samples were cut into cylindrical shape to fit in the crucibles, and the crucibles were placed in silica tubes $\frac{3}{8}$ in. in diameter. The tubes were reduced in diameter to about $\frac{1}{4}$ in. at a distance 4 in. from the bottom, and were attached to a high-vacuum pump. The pressure was reduced to approximately 0.001 mm. of mercury, the sample was brought to a little above its melting point, to drive out dissolved gases, and the top of the tube was sealed off. The silica tubes were then lowered into a resistance furnace. A temperature difference of 15° to 20°C . was provided between the top and the bottom of the silica tubes, to prevent the accumulation of the magnesium vapor on the top of the tubes. The samples were held for $\frac{1}{2}$ hr. at the desired temperature, then taken from the furnace and cooled in an air blast projected at a constant rate to the bottom. After solidification had been completed, the tubes were broken and the average grain size of the solids at proper sections was determined.

For comparison, another set of samples was prepared under the same conditions, except that the melting and solidification were carried out under a melting flux in the presence of air with open silica tubes.

Table 5 shows the average grain size of the castings. Superheating magnesium alloys in the presence of air, as well as in vacuum, produces an appreciable grain refinement. When melted in vacuum, magnesium vapors rising above the molten alloy, particularly at high temperatures, reacted with silica to form a thin film of magnesium silicide on the walls of the container; some of the vapor also condensed on the walls during solidification. The metal thus lost probably caused a shift in the composition of samples. The percentage loss was, however, not very large (from 5 to 11 per cent), and the effect of the shift in composition on grain

size could be neglected. The addition of flux to samples melted in vacuum had no appreciable effect on grain size.

It is apparent that the grain-refining effect of superheating cannot be attributed to variations in the gas content of magnesium alloys, a hypothesis that was pointed out as a possibility by Achenbach, Nipper and Piwowarsky.⁵

TABLE 5.—Average Grain Size of Magnesium Alloys Melted in Vacuum and in the Presence of Air

Alloy Composition, Wt. Per Cent	Melting Medium	Super- heating Temp., Deg. C.	Grains per Sq. Mm.
5.7 Al-2.9 Zn-0.33 Mn	air	680	7
	air	870	32
	vacuum	680	20
	vacuum	870	40
	vacuum	870	45
8.6 Al-2.0 Zn-0.3 Mn	air	680	20
	air	870	65
	vacuum	660	25
	vacuum	750	45
	vacuum	870	70

Bubbling Various Gases through Superheated Melts

Elimination of dissolved gases from magnesium alloys by melting in vacuum showed no appreciable effect on grain size. A logical continuation of the experiments would be to examine the effect of bubbling various gases through molten alloys upon the grain size of castings. The work was limited to carbothermic A.S.T.M. No. 17 alloy, and to bubbling of hydrogen, nitrogen, chlorine and helium.

A stream of hydrogen from a high-pressure cylinder was passed through the molten alloy by means of an iron tube extending to the bottom of the crucible. The passage of hydrogen was sufficiently rapid to produce the effect of a moderate ebullition of the melt, without ejection of liquid from the crucible, and the temperature of the melt was 700° , 750° , 820° , 875° and 920°C ., respectively. After hydrogen had been bubbled for about $\frac{1}{2}$ hr., the crucible was taken from the

furnace and the melt poured immediately into graphite mold. Visual inspection of the longitudinal sections of the cones showed that the castings from 700° and

on the surface of the alloy, and chlorine, magnesium chloride. These compounds are always present in small amounts in the melt as a result of the reaction with



FIG. 2.—LONGITUDINAL SECTIONS OF TEST CONES OF A CARBOTHERMIC NO. 17 MAGNESIUM ALLOY, ILLUSTRATING EFFECT OF BUBBLING HYDROGEN THROUGH MELTS AT VARIOUS TEMPERATURES. $\times \frac{1}{8}$.

a, 700°C.; *b*, 750°C.; *c*, 820°C.; *d*, 875°C.; *e*, 920°C.

750°C. exhibit very little visible cavities (blowholes), while the others contain a large number of cavities (Fig. 2). It is, therefore, evident that hydrogen is dissolved in the molten alloy in increasing amounts with temperature, and that upon cooling the alloy became super-saturated and the excess gas is set free.

The castings made by bubbling hydrogen through the molten alloy had somewhat finer grains than those made without bubbling gas, particularly at small sections. It is, however, not certain whether this grain refinement is due to the influence of hydrogen set free during cooling upon the process of crystallization, or the presence of large cavities causes a change in the cooling rate and thus indirectly affects the grain size.

No effect was noted on grain size of the castings obtained by bubbling nitrogen, chlorine and helium through the molten alloy at high temperatures. Nitrogen forms a brown "scum" (magnesium nitride)

the air and the contamination with fluxes. The results indicate that an increase in the formation of these compounds has no appreciable effect on grain size.

The passage of an inert gas (insoluble and chemically inactive), such as helium, through molten alloy may cause the removal of dissolved gases from the alloy, as has been shown by Archbutt,⁷ Tullis,⁸ Rosenhain and his associates⁹ for molten aluminum and its alloys. This procedure has, therefore, no effect on the grain size of magnesium alloys, a fact that agrees with the results on superheating in vacuum.

Deoxidation of Superheated Melts before Casting

These experiments deal with the effect of the deoxidation of superheated melts upon the final grain size of castings. The work was limited to carbothermic A.S.T.M. No. 4 alloy (5.7 per cent aluminum, 2.9 zinc and 0.33 manganese), and to the use

of lithium and potassium as deoxidizing media.

A 300-gram sample of the alloy was melted and refined with flux in graphite crucible. The melt was heated for 10 min. at 870°C., then the crucible taken from the furnace and cooled in still air. When the temperature reached 735°C., lithium or potassium, in amounts ranging from 1 to 2 grams, was submerged into the melt, and vigorously stirred for about ½ min. The deoxidizing metal was placed in small cylinders of No. 4 alloy attached to the stirring rod and the rod was submerged quickly into the melt, so that no reaction between the deoxidizing metal and the atmosphere had taken place. The alloy cylinders remained solid during the short period of stirring. When stirring had been completed, the melt was cooled to 700°C. and immediately poured into graphite mold. This procedure was repeated without using deoxidizing metal for control purposes, and also under a sulphur dioxide atmosphere by dusting on sulphur to the melt surface.

The measurements of grain size of castings showed that the deoxidizing of No. 4 alloy with lithium or potassium under a cover of flux or sulphur dioxide atmosphere has little refining effect in large sections of the cones or no effect at all on grain size.

Alloying Constituents and Superheating Effect

These experiments were intended to study the dependence of the superheating effect on the alloying constituents of magnesium. The samples, weighing approximately 200 grams, were taken from a pure carbothermic magnesium ingot or from alloy ingots, prepared under similar conditions with pure carbothermic magnesium and alloying materials, and were melted in graphite crucible under a protecting flux. One series of samples were heated for ½ hr. at 700°C. and then cast at that temperature into graphite mold of 300°C. Another

series of samples were heated for ½ hr. at 850°C., then the crucibles were taken from the furnace, cooled to 700°C. in still air and the melts were immediately poured into graphite mold of 300°C.

The results of grain-size testing are shown in Table 6. The superheating effect

TABLE 6.—Average Grain Size of Various Normal and Superheated Magnesium-rich Alloys

Alloy Composition, Wt. Per Cent	Melt Tem- perature, Deg. C.	Grains per Sq. Mm.	
		Small Section	Large Section
Pure Mg.....	700	Coarse grains	columnar
Pure Mg.....	850	Coarse grains (as above)	columnar
2 Mn.....	700	Columnar grains	
3 Mn.....	700	Columnar grains (as above)	
9 Al.....	700	35	25
9 Al.....	850	60	40
3.0 Zn.....	700	15	10
3.0 Zn.....	850	14	12
6.0 Zn.....	700	32	25
6.0 Zn.....	850	30	23
10 Al-0.3 Mn.....	700	35	25
10 Al-0.4 Mn.....	850	180	150
3.0 Zn-0.1 Mn.....	700	15	12
3.0 Zn-0.1 Mn.....	850	15	10
6 Zn-1 Mn.....	700	30	20
6 Zn-1 Mn.....	850	25	16
6 Al-3 Zn.....	700	40	30
6 Al-3 Zn.....	850	80	62
5.7 Al-2.9 Zn-0.33 Mn.....	700	35	30
5.7 Al-2.9 Zn-0.33 Mn.....	850	120	95
8.6 Al-2.0 Zn-0.3 Mn.....	700	40	32
8.6 Al-2.0 Zn-0.3 Mn.....	850	280	250

is not noticeable in pure magnesium, magnesium-manganese, magnesium-zinc, and magnesium-zinc-manganese alloys, but is apparent in magnesium-aluminum and magnesium-aluminum-zinc alloys, and the effect is considerably increased by the addition of small quantities of manganese to these two alloys.

Pure magnesium and magnesium-manganese binary alloy exhibited columnar grained structures and no accurate grain-size measurements could be made. The macrographs of large sections of these castings are shown in Figs. 3 and 4. The grains of magnesium-manganese binary alloy appear to be somewhat smaller than those of pure magnesium, but in both

castings no appreciable effect of superheating on grain size is noticeable. Magnesium-manganese alloy castings were made from a pre-alloy containing 3 per cent

Magnesium ingots used in the preparation of the alloys were very pure and contained approximately 0.001 per cent iron, 0.01 calcium, 0.01 lead, 0.005 silicon, 0.000

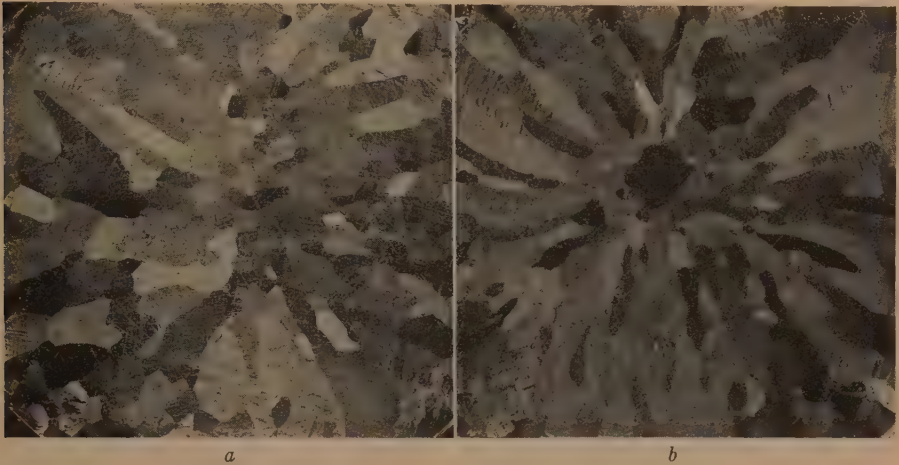


FIG. 3.—CROSS SECTIONS OF PURE MAGNESIUM TEST CONES. ETCHED IN PICRIC-ACETIC ACID ETCHANT. $\times 2$.

a. Heated at 700°C. for $\frac{1}{2}$ hour.

b. Superheated at 850°C. for $\frac{1}{2}$ hour.

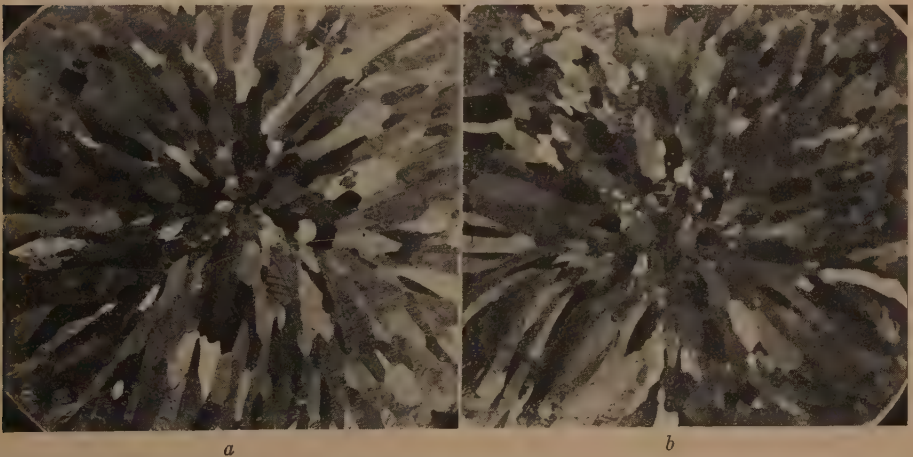


FIG. 4.—CROSS SECTIONS OF MAGNESIUM-MANGANESE ALLOY TEST CONES. ETCHED IN PICRIC-ACETIC ACID ETCHANT. $\times 2$.

a. Heated at 700°C. for $\frac{1}{2}$ hour.

b. Superheated at 850°C. for $\frac{1}{2}$ hour.

manganese. Upon remelting, the manganese content of the superheated alloy remained practically constant, whereas that of the normal alloy dropped to 2 per cent.

copper, 0.000 nickel and 0.000 manganese. Commercial zinc was also of satisfactory purity, but aluminum contained too much iron (about 0.15 per cent). Attempts were

made to determine whether the presence of iron in the castings has any effect on grain size. The effect of manganese additions was also studied in more detail.

Table 7 shows the grain size of magnesium alloys containing 9 to 10 per cent aluminum and various amounts of iron or manganese. Aluminum used in the preparation of these samples was high-purity aluminum. Iron was added by stirring iron powder into the molten alloy, and manganese through the use of a prealloy made by reducing pure $MnCl_2$ with pure magnesium. Chemical and spectrographic analyses of the samples are also given. It is to be noted

Furthermore, the superheating effect is more or less increased with increasing amounts of iron or manganese. Because of the difficulties in determining and controlling the exact size of the grains, the study of the superheating effect as a function of iron or manganese content was semiquantitative, and no sharp tolerance limits for iron or manganese were established. However, attempts were made to determine accurately the liquid solubility of manganese or iron in magnesium-aluminum alloys as a function of temperature. The results concerning the solubility of manganese was reported in an earlier

TABLE 7.—*Magnesium-aluminum Alloys Containing Various Amounts of Iron or Manganese*

Ingot No.	Average Grain Size			Wet Analysis, Per Cent			Spectrographic Analysis, Per Cent				
	Superheating Temperature, Deg. C.	Grains per Sq. Mm.									
		Small Section	Large Section	Al	Mn	Fe	Si	Ca	Pb	Cu	Zn
1	700	34	25	9.0		0.013	0.005	0.001	0.001	0.002	0.005
2	850	30	25	8.9		0.001	0.001	0.002	0.001	0.001	0.005
3	860	68	40	9.8		0.032	0.01	0.001	0.001	0.0005	0.005
4	850	85	56	8.9		0.050	0.01	0.005	0.005	0.005	0.005
5	700	45	30	8.7	0.02	0.012	0.005	0.001	0.001	0.005	0.001
6	850	52	40	9.1	0.02	0.015	0.01	0.001	0.001	0.002	0.001
7	700	34	25	10.3	0.16	0.010	0.01	0.001	0.002	0.0005	0.005
8	850	170	130	10.2	0.19	0.015	0.02	0.001	0.001	0.0005	0.005
9	850	208	164	10.2	0.48	0.020	0.03	0.001	0.001	0.0005	0.005
10	850	290	242	9.8	0.98	0.020	0.02	0.001	0.001	0.0005	0.005

that: (1) magnesium-aluminum alloys show no appreciable superheating effect when prepared from high-purity alloying materials, particularly when iron content is 0.001 per cent or less; (2) magnesium-aluminum alloys containing 0.03 or more iron show some grain refinement on superheating; and (3) the addition of 0.02 per cent manganese to magnesium-aluminum alloys has little or no effect on grain size, while the addition of 0.19 per cent or more manganese causes considerable grain refinement on superheating.

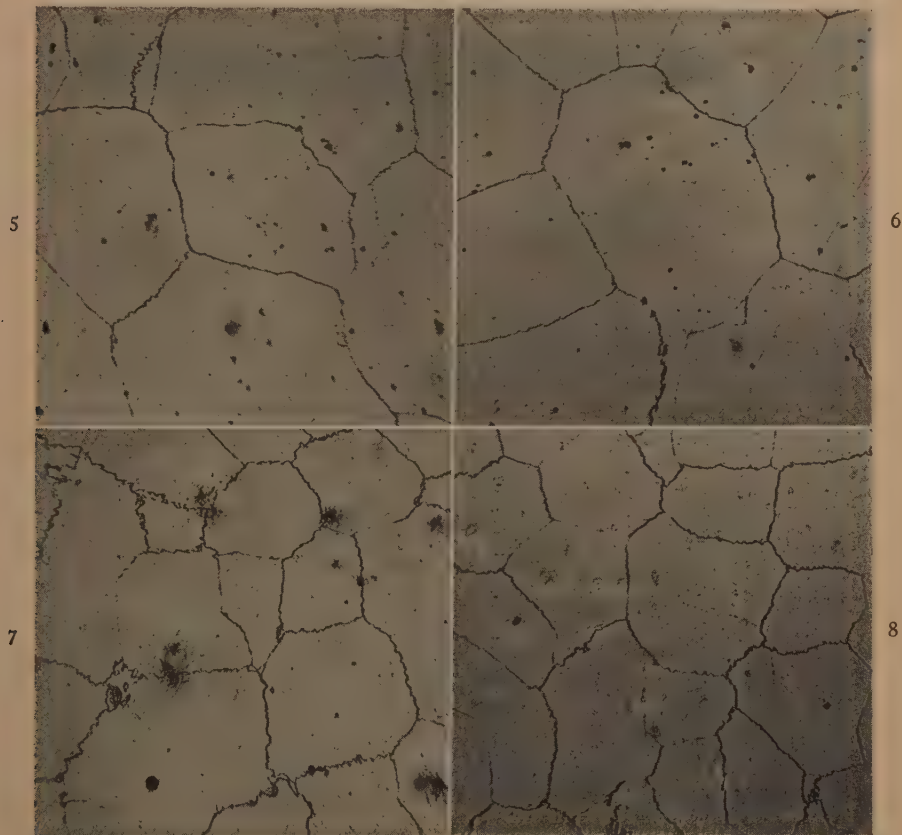
Magnesium-aluminum alloys appear to exhibit superheating effect if they contain iron or manganese above certain limits.

work.¹⁰ It is sufficient to note here that the solubility of manganese or iron in liquid magnesium decreases with increasing aluminum contents and increases with increasing temperature. Near the freezing point, magnesium alloys containing about 8 per cent aluminum can dissolve approximately 0.1 per cent manganese, and those containing 9 per cent aluminum can dissolve approximately 0.005 per cent iron.* Examination of the data on grain size in the light of these findings reveals that magnesium-aluminum alloys exhibiting super-

* These results are approximate and are found by extrapolating curves for the logarithm of solubility vs. reciprocal temperature.

heating effect contain iron or manganese in amounts above the solubility limit of these elements in the molten alloys near the freezing point.

manganese and iron appear as separate constituents (inclusions) within the grains (see Figs. 13 and 14). The number of inclusions observed under the microscope seems



FIGS. 5-8.—MAGNESIUM ALLOYS. $\times 150$.*

Fig. 5. Containing 9.0 per cent aluminum 0.013 per cent iron. Heated at 700°C . for 30 minutes; 34 grains per sq. mm.*

Fig. 6. Containing 8.9 per cent aluminum, 0.001 per cent iron. Superheated at 850°C . for 30 minutes; 30 grains per sq. mm.

Fig. 7. Containing 9.8 per cent aluminum, 0.032 per cent iron. Superheated at 860°C . for 30 minutes; 68 grains per sq. mm.

Fig. 8. Containing 8.9 per cent aluminum, 0.050 per cent iron. Superheated at 850°C . for 30 minutes; 85 grains per sq. mm.

The micrographs (Figs. 5 to 12) illustrate the effect of various amounts of iron or manganese on grain size of magnesium-aluminum alloys in small sections. Both

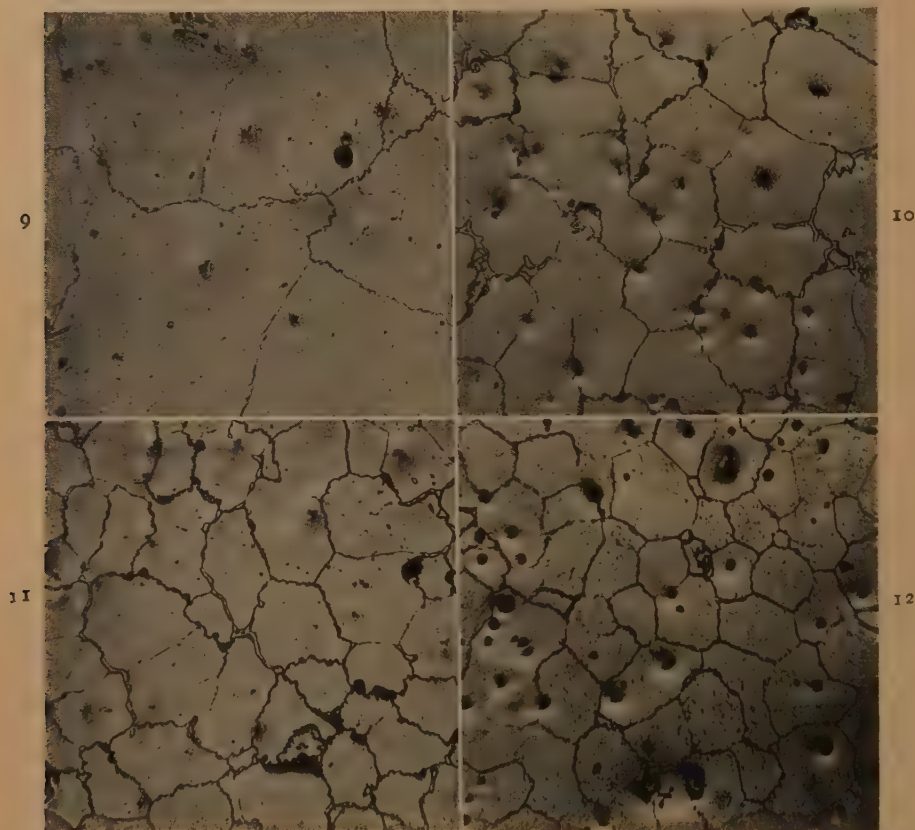
* Samples of Figs. 5 to 12 homogenized and etched in glycol etchant. Grain-size estimates refer to the small sections of test ingots and to a much larger surface area than is included on these micrographs.

to have no definite relation to grain size; the areas containing higher manganese or iron concentration (segregation) had practically the same grain size as those containing lower concentration.

The addition of small amounts of iron to No. 4 alloy showed no additional increase in the superheating effect. The No. 4

alloys containing 0.5 per cent silicon or 1 per cent antimony or cobalt had somewhat finer grains on superheating than the base No. 4 alloy.

Nipper and Piwowarsky.⁵ The experiments now to be described were intended to extend this thermal analysis to pure magnesium, and to magnesium-aluminum and



FIGS. 9-12.—MAGNESIUM ALLOYS. $\times 150$.

Fig. 9. Containing 9.1 per cent aluminum, 0.02 per cent manganese, 0.015 per cent iron. Superheated at 850°C. for 30 minutes; 52 grains per sq. mm.

Fig. 10.—Containing 10.2 per cent aluminum, 0.19 per cent manganese, 0.015 per cent iron. Superheated at 850°C. for 30 minutes; 170 grains per sq. mm.

Fig. 11.—Containing 10.2 per cent aluminum, 0.48 per cent manganese, 0.020 per cent iron. Superheated at 850°C. for 30 minutes; 208 grains per sq. mm.

Fig. 12.—Containing 9.8 per cent aluminum, 0.98 per cent manganese, 0.020 per cent iron. Superheated at 850°C. for 30 minutes; 299 grains per sq. mm.

Superheating and Undercooling

The relationship between superheating and subsequent undercooling for magnesium-aluminum and magnesium-aluminum-zinc alloys has been investigated, with great precision, by Achenbach,

magnesium-aluminum-zinc alloys containing small quantities of manganese.

The specimens, weighing approximately 80 grams, were melted in a graphite crucible, 2 in. high and $1\frac{1}{4}$ in. in diameter. The temperature was brought to the de-



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FIG. 13.—TYPICAL APPEARANCE OF MANGANESE CONSTITUENT OF A MAGNESIUM ALLOY (10.0 PER CENT Al, 0.3 PER CENT Mn) CASTING. UNETCHED. $\times 1000$.

FIG. 14.—TYPICAL APPEARANCE OF IRON CONSTITUENT OF A MAGNESIUM ALLOY (9.8 PER CENT Al, 0.032 PER CENT Fe) CASTING. UNETCHED. $\times 1000$.

sired point, then, the crucible was taken from the furnace and allowed to cool in still air. A small iron-constantan thermocouple, insulated with a thin sodium chloride film (m.p. $804^{\circ}\text{C}.$), was dipped into the melt. The salt film was prepared by dipping the thermocouple into a molten sodium chloride bath, and the actual junction was left in direct contact with the molten metal. The small mass and heat capacity of thermal elements provided a great sensitivity, so that a small evolution of heat accompanying phase changes was detectable.

The thermocouple was connected to a Leeds and Northrup precision potentiometer, which was provided with a sensitive mirror galvanometer having a temperature range of about $10^{\circ}\text{C}.$ (4 divisions per degree). First curves for time vs. temperature were manually recorded to determine liquidus points; then the potentiometer current was set at the values corresponding to liquidus points, and the deflection of the galvanometer was noted. During cooling the temperature drops uniformly, and a sudden rise in temperature, associated with undercooling, is indicated by a backward deflection of the galvanometer. With a few trials, it was possible to adjust the potentiometer current properly and to read the magnitude of this backward deflection on the dial.

The degree of undercooling of the specimens superheated to various temperatures and the grain size of the resultant and solids are shown in Table 8. The measurements of undercooling for a given thermal treatment of the melt are not completely consistent, particularly for pure magnesium. It is not certain whether this is due to an inherent probability factor in the process of formation of nuclei, as is suggested by the experiments of Lange,¹¹—who finds that the formation of nuclei in zinc, cadmium and lead for a given amount of undercooling is an exponential function of time—or that the control of conditions in these

experiments is inadequate. Qualitatively, however, it can be stated that in the pure magnesium and magnesium-zinc alloy there is no definite correlation between the temperature of superheating and the amount of subsequent undercooling, while in the magnesium-aluminum-manganese and magnesium-aluminum-zinc-manganese alloys, superheating tends to decrease the magnitude of subsequent undercooling.

TABLE 8.—*Undercooling and Grain Size of Pure Magnesium and Magnesium-rich Alloys*

Alloy Composition, Wt. Per Cent	Superheating Temp. $^{\circ}\text{C}.$	Undercooling		Grains per Sq. Mm.
		Number of Divisions on the Dial	Estimated Temperature, Deg. C.	
Pure Mg.	700	4	1.0	0.05–0.06
	700	2	0.5	
	700	3	0.75	
	850	3	0.75	0.05–0.06
	850	1.8	0.45	
	850	3.5	0.88	
4 Zn	700	1.5	0.38	2–3
	700	1.0	0.25	
	700	1.2	0.30	
	850	1.0	0.25	2–3
	850	2.0	0.50	
	850	0.8	0.20	
9 Al-2 Zn-0.15 Mn	700	1.5	0.38	5
	700	2.0	0.50	
	850	0.5	0.12	
	850	0.2	0.05	10
	700	3.0	0.75	
	700	2.5	0.62	
9 Al-0.2 Mn.	700	2.0	0.50	8
	850	1.0	0.25	
	850	0.8	0.20	
	850	1.0	0.25	

The grain size of pure magnesium and magnesium-zinc alloy shows no appreciable change on superheating, whereas that of magnesium-aluminum-manganese and magnesium-aluminum-zinc-manganese alloys tends to decrease. This grain refinement is associated with a decrease in the degree of undercooling in agreement with thermal analysis of Achenbach, Nipper and Piwowarsky. Owing to slow cooling, the grain size of the specimens was large, and the grain refinement on superheating was not pronounced, as in the alloy castings previously reported.

ATTEMPTS TO EXPLAIN THE SUPERHEATING EFFECT ON GRAIN SIZE

According to the crystallization theory developed by Tammann^{12,13} the grain size of a cast metal or alloy is determined by the rate of spontaneous formation of nuclei and the rate of crystal growth. Whenever the latter, for any reason, becomes the more predominant factor in the solidification process, there are relatively few centers of crystallization, but these few nuclei grow rapidly into a few large grains, and the resultant solid will possess a generally coarse-grained structure. On the other hand, if the rate of nucleation is rapid as compared with the growth rate, a large number of growing grains marks the progress of solidification almost from the start, and the final solid will be fine-grained.

Molten metals or alloys may frequently contain foreign particles and/or crystal residues from the stable condition before melting, which act as nuclei for crystal growth. Since the number of spontaneously formed nuclei will be augmented by these crystallization centers, the structure of the final solid in this case will be dependent on the number of crystallization centers preexisting in the melt at the freezing point, as well as the relative predominance of the rates of spontaneous nucleation and crystal growth. Superheating effect on grain size of cast metals or alloys has been ascribed by various investigators almost exclusively to the influence of these preexisting nuclei upon the course of crystallization. In an attempt to explain the grain refinement of magnesium alloys by superheating, the following train of thought may be disclosed:

1. The superheating effect on grain size of magnesium alloys can be attributed neither to metal lattice residues from the stable condition before melting, as proposed by Mitsche¹⁴ for pure aluminum, nor to crystalline adsorption layers persisting on impurities, as suggested by Richards¹⁵ for salol and other substances. For these metal residues or adsorption layers on im-

purities would progressively be destroyed with increasing temperature of superheating, and hence the magnitude of undercooling during subsequent cooling would be increased with superheating temperature, and also the time of holding the melts at low temperatures before casting would have no neutralizing effect on superheating. Both of these effects are not confirmed by the present experimental work. It is, therefore, reasonable to assume that the foreign particles (minor constituents) are largely responsible for the superheating effect.

2. The minor constituents of a melt that may act as crystallization centers may be dissolved gases set free during solidification, metallic or nonmetallic particles in solid or liquid form. The absorption of gases and the formation of reaction gases are in general increased by superheating. During subsequent cooling they may be supersaturated and set free, and possibly affect the course of crystallization, as pointed out by Achenbach, Nipper and Piwowarsky.⁵ The removal of dissolved gases from magnesium alloys by melting in vacuum or by the passage of an inert gas, such as helium, through the melt, does not suppress the superheating effect. Consequently, it is not feasible to assume that dissolved gases are of major importance in the grain refinement of magnesium alloys by superheating. Bubbling hydrogen through a melt at elevated temperatures produced some grain refinement, but no definite conclusion could be reached regarding the mechanism of this effect.

3. Suspended liquid slag particles or insoluble solid particles present in the melt preferentially flow together or separate from the melt at high temperatures, because of decrease in viscosity.¹⁶ In such cases, the preexisting crystallization centers in the melt should be reduced, and the undercooling tendency of the melt in subsequent cooling should be increased. Thermal analysis shows that superheating

of magnesium alloys is not accompanied by an increase but by a decrease in the magnitude of undercooling. Therefore, a direct nucleating action of suspended liquid slag particles or completely insoluble solid particles cannot be expected.

4. Against the possibility that at the higher melt temperatures a reduction of minor constituents can take place and otherwise possible nuclei formation is thus decreased, one may cite the argument imparted in the previous paragraph; namely, the decrease in the magnitude of undercooling by previous superheating.

5. At the higher melt temperatures there can be an increased oxidation (or nitridation), leading to an increase in the number of nonmetallic particles. However, this assumption is not easily reconciled with the facts that pure magnesium, magnesium-zinc and extremely pure magnesium-aluminum alloys do not show any appreciable grain refinement by superheating. Furthermore, avoiding the formation of oxide and nitride inclusions by melting in a vacuum or destroying these inclusions by treatment with a powerful deoxidizing agent such as lithium, or potassium, does not reduce the effect of superheating on grain size of the alloys.

6. It is, therefore, probable that the superheating effect depends largely on an influence of solid soluble minor constituents upon the course of crystallization. This hypothesis is substantiated by thermal analysis and by the fact that when sufficient time is allowed for the establishment of equilibrium conditions, the superheating effect will be independent of the previous thermal treatment of the melt and will be the same, within certain limits, whether the melt is brought to the desired temperature from lower or from higher temperatures.

According to Achenbach, Nipper and Piwowsky,⁵ some material that at normal temperatures is too large in particle size to be effective is taken into

solution at the high temperatures, and reprecipitates to form fine nuclei during the cooling process, thus causing a grain refinement. If the melt stands for some time at low temperatures before casting, the precipitated particles coagulate or grow so that a favorable action on grain size can no longer be expected. The attempts made in the present work to determine the nature of the solid soluble material responsible for the superheating effect indicate that manganese and iron are important in this connection. Magnesium-aluminum alloys containing very small amounts of iron or manganese do not show any appreciable superheating effect, whereas those containing iron or manganese above the solubility limit near the freezing point of the base alloy show a more or less pronounced grain refinement by superheating. The addition of manganese to pure magnesium and magnesium-zinc alloy seems to have no effect on grain size, and the presence of aluminum in the alloys seems to create a favorable condition for the superheating effect.

The crystallization of magnesium-aluminum alloys containing manganese or iron begins with the formation of a manganese or iron phase. This is followed by the solidification of the parent solution of aluminum (and probably some manganese or iron) in magnesium. It may be assumed that superheating causes molten alloy to dissolve a greater amount of manganese or iron and to become supersaturated upon subsequent cooling. These supersaturated alloys have large nucleation rates, and form fine-grained structures. If the alloys are heated at low temperatures or are allowed to stand at low temperatures after superheating, little or no supersaturation occurs before freezing and the molten alloys tend to form a small number of crystallization centers. One may call attention here to the Von Weimarn equation for the initial rate of precipitation from solutions.¹⁷ According to this equation

$$W = K \frac{Q - L}{L}$$

where W is the initial rate of precipitation, Q the total concentration of the substance that is to precipitate, L its solubility, and K a constant. Among the several factors that are lumped together in the constant K are: the effect of the viscosity of the precipitation medium, adsorption, the presence of solid particles, the presence of turbulence, the specific tendency to form nuclei and the specific tendency to grow on nuclei. Superheating seems to increase the absolute supersaturation $Q-L$ and the constant K so that the initial rate of precipitation of manganese or iron is increased and thus a fine-grained structure is produced.

In the course of crystallization, some of the manganese particles precipitated probably do not nucleate the parent grains, and tend to grow and to segregate; some of the parent grains also form independently. As a result, the microscopic observations do not show definite correlation between grain size and the number of manganese particles. The nucleating action of manganese in pure magnesium and magnesium-zinc alloy seems also to be of no importance.

The dependence, within certain limits, of the final grain size upon the structure of the charge can be attributed to the presence of persisting nuclei in the melt. These nuclei probably are fortuitous products due to manganese, iron or other local impurities in the parent grain. Increasing temperature of superheating causes these products to dissolve in or to separate from the melt, and thus eliminates the effect of the structure of the charge on grain size.

The hypothesis of the influence of solid soluble minor constituents upon the course of crystallization forms a satisfactory explanation for the phenomena observed in superheating of magnesium alloys. There is, however, one objection that

might be considered—although the solubility of solids in a melt in general increases continually with temperature, superheating the alloys to very high temperatures (980°C. or more) tends to produce a grain coarsening. The attempts made in the present work to determine the nature of the minor constituents responsible for the superheating effect are limited, and further investigations are to be made in this connection.

SUMMARY

The effects of various superheating conditions upon the grain size of magnesium casting alloys have been investigated and the following observations have been made:

1. The grain refinement of magnesium alloys by superheating is maximum at a certain temperature range between 850° and 900°C., and at higher temperatures of superheating there is a tendency for grain coarsening.

2. Superheating molten alloys for several hours at low temperatures produces some grain refinement, but as the superheating temperature is raised to about 850°C., the time required to get the full effect drops off to zero.

3. (a) The superheating effect on grain size is gradually and completely neutralized by holding the molten alloys for increasing periods of time at low temperatures before casting.

- (b) When the molten alloys are held at a given temperature for a sufficient length of time, the resultant grains exhibit, within certain limits, the same size whether the melts are brought to the desired temperature from lower or from higher temperatures.

4. Stirring the molten alloys at about 800°C. causes a considerable grain refinement, but when stirring is carried out at 700°C. the resultant solid generally has coarser grains.

5. All other factors being practically

constant, the grain size of an alloy varies, within certain limits, with the structure of the charge before melting; this variation in grain size is noticeable when the melts are superheated at low temperatures for short period of time, but decreases and completely disappears as the superheating temperatures is increased.

6. Repeated superheating of the melts at elevated temperatures (850° to 900°C.) does not produce any appreciable change in grain size of resultant castings.

7. The superheating effect on grain size can be suppressed neither by carrying out the melting operations in vacuum, nor by treatment with a powerful deoxidizing agent such as lithium or potassium

8. Bubbling nitrogen, chlorine and helium through superheated alloys has no appreciable effect on grain size, whereas bubbling hydrogen produces a relatively fine-grained structure with numerous blow-holes.

The superheating effect on grain size has been observed in magnesium-aluminum or magnesium-aluminum-zinc alloys containing manganese or iron, but not in pure magnesium, magnesium-zinc, magnesium-manganese and extremely pure magnesium-aluminum alloys. The effect is found to be associated with a decrease in the undercooling capacity of the alloys.

Attempts are made to explain the experimental results. The hypothesis that the superheating effect on grain size is related to the influence of solid soluble minor constituents upon the course of crystallization is found in general satisfactory.

ACKNOWLEDGMENTS

The experimental work was carried out by the author in the Permanente Metals Laboratory, and in the Metallurgical Laboratories of Stanford University and University of California at Berkeley. Chemical and spectrographic analyses were made by members of the Permanente Metals Laboratory.

The author wishes to thank Prof. O. C. Shepard for his suggestions and for his help with the manuscript; Dr. W. O. Wetmore and other members of the Permanente Metals Laboratory; and Dr. R. R. Hultgren, of the University of California, for their assistance in the experimental work.

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DISCUSSION

(C. E. Nelson presiding)

R. S. BUSK.*—The present paper is an excellent contribution to the problem of the superheating of magnesium alloys. The author is to be congratulated on a careful and thorough piece of work. The following comments are made as substantiation of much of Mr. Tiner's work, together with some comment on the conclusions.

We have found also that holding A.S.T.M. 17 alloy at 980°C. will cause a coarsening of the grain size. We have found that this effect is first noticeable at about 925°C. In agreement with the author, we have found also that the grain-size characteristic of a given superheating temperature is independent of the direction of approach to that temperature.

Considerable work in this laboratory on the effects of gases on magnesium alloys confirms the fact that the presence or absence of hydrogen in amounts below the "bubble" stage is of no importance to grain size.

Considerable weight is given to the lack of complete grain refinement in the absence of manganese. It has been shown¹⁸ that the presence of manganese is important for minimizing grain growth during heat-treatment. The author's rather extensive heat-treatments before measurement of grain size suggest that the role of manganese may be more that of prevention of grain growth in the solid than of nucleation of grains in the liquid. Does examination of the grain size of the manganese-free specimens in the as-cast state confirm the measurements made after heat-treatment?

J. R. SCRIVENER.†—Do you think that the presence of graphite, principally in the crucible material would affect the grain-size results?

Is the large grain size obtained in commercial practice, where large melts of up to 2 tons are used, due to the slower cooling rates obtained during cooling to the pouring temperature after superheating or refining?

I believe that it has been found that iron contents of more than 0.005 per cent decrease

the corrosion resistance. Do you know whether there is any connection between the iron content for maximum corrosion resistance and the minimum iron content to obtain grain refining?

J. ALICO.*—The author of the paper points out that the effects of superheating are not carried forward through subsequent remelting operations. Going beyond the scope of this paper, I wondered if in your own work, Mr. Nelson, you have ever found that subsequent remelting and further superheating have had any effect on the mechanical properties of the metal?

C. E. NELSON.†—Your question is not very clear to me. What do you mean?

J. ALICO.—Was there any breakdown of the structure due to subsequent superheating? In other words, more than one superheating?

C. E. NELSON.—Is there any other discussion?

C. H. LORIG.‡—I think the paper is excellent and covers the subject of superheating and its effect on grain size of aluminum-containing alloys of the cast type very well indeed.

I do want to bring up one point, however; it is recognized now that treating aluminum-containing magnesium alloys with carbon is very effective in controlling grain size without the need for superheating. It brings up the question whether the melting of the alloys in graphite crucibles and the use of carbothermic magnesium, which contains carbon, did not influence also the grain refinement attributed in the paper to superheating alone.

The grain-refining effect of the carbon treatment tends to carry over when using in melts scrap or magnesium-alloy pig that have previously been treated with carbon. Castings of aluminum-magnesium alloys made from charges containing carbon-treated metal invariably show grain refinement without further treatment with carbon or superheating. An interesting side light on grain-size control of magnesium with carbon is that the treatment is effective only in the alloys containing

* Dow Chemical Co., Midland, Michigan.

¹⁸ A. T. Peters, R. S. Busk and H. E. Elliott: Factors Affecting Abnormal Grain Growth in Magnesium Alloy Castings. *Trans. A.I.M.E.* (1944) 161, 291.

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‡ Battelle Memorial Institute, Columbus, Ohio.

aluminum; neither the manganese-magnesium nor the zinc-magnesium alloys can be refined with carbon.

MEMBER.—Will carbon or the introduction of a gas or superheating have the same effect on the wrought alloys that are cast in the continuous machine? Would the effect be as great as it is in sand-casting alloys?

C. E. NELSON.—I think I might start backward here by trying to answer that last question while it is still fresh. We find that while the same principles hold on the wrought alloys as on the cast as far as grain refining is concerned and superheating, it is a good bit more difficult to apply ordinary grain-refining techniques to the casting of large ingots by direct chill or continuous casting, which is, I believe, what you are referring to.

However, I think it is safe to say that the same methods are somewhat effective and you will just have to be a little bit more careful; that is, it is more difficult to obtain the grain refinement. Part of the reason for it is that in nearly every case very large pots are used, and one of the comments I wanted to make, which I think has a bearing on this question, is that almost all of this work was on very small crucibles; around, I believe, 120 to 200 grams. In all of our work on grain refining we have found that treatments that would work in small crucibles may be much more difficult on a larger scale, and often things that would work on a small scale will not work at all, say, on 1-ton or 2-ton pots.

The direct answer, I think, to your question of grain refining of billets is that by carbon addition or agitation or treatment with carbon-containing materials it is possible to refine the grain of billet alloys.

I think I have probably answered the question about the large-size melts, the 2-ton melts, that was asked a few minutes ago. There is just one additional point in that connection. I do not believe that the rate of heating in bringing the pot to superheating temperatures is of great consequence, but the rate of subsequent cooling, if the pots are to be brought up to superheating temperatures by conventional means, would be too slow. In other words, if you were going to refine the grain at 900°C., and were going to pour the metal off at 700° or

750°C., the rate of cooling to that temperature would be so slow that most if not all of the grain-refining effect would be lost.

With respect to the question of the harmful effect of repeated superheating, I can only say that we have given that considerable study and we have never been able to see any harmful effect of repeated superheating on corrosion or properties or on the ability to get refinement of the grain. In other words, we see no harmful effect of repeated superheating.

The corollary to that is that we see no advantage to repeated superheating. If the metal is to be superheated once, and if you want to be really sure of a good quality casting, we think that the best time to do it is pretty shortly before pouring. Do not depend on the previous history.

With respect to the question of whether alloys with the low iron content (< 0.005 per cent) required to give maximum salt-water corrosion resistance can still be superheated, I will say that it is possible to refine the grain even in high-purity magnesium alloys, and I think probably the answer is that while the iron is absent in this case, the manganese is still present and, just borrowing Mr. Tiner's theory for the moment, and assuming that it is right, I think the manganese can take control in this case. It is certainly possible to make high-purity wrought alloys or cast alloys with iron say a thousandth of a per cent or less and still get fine grains.

Dr. Lorig's remarks on the use of carbon crucibles would logically be something of a criticism of this work, I think. However, I do not believe we ought to take it too seriously or consider it too much of a limitation here, because a great deal of work has been done by a number of people using graphite crucibles and steel crucibles, and the main difference observed was that while there may be some slight beneficial effect of the carbon picked up from the crucible, it shows only a tendency to lower slightly the temperature at which superheating effects are obtained. At least, that is our experience and I believe the experience of others in the field. The general behavior in using graphite crucibles would, as far as our information is concerned, be the same that would be obtained with a steel crucible.

One other comment I would like to make with respect to Dr. Lorig's remarks.

While we feel that carbon additions are one very good way in which to get grain refinement in magnesium alloys, I would like to introduce a note of caution again in connection with assuming that the grain size of alloys can be refined by addition of carbon and remelting of that material and positively obtaining fine grain without some additional superheating treatment.

In other words, it comes back to the practical case, if you are operating a foundry and must get fine-grained castings, you are not allowed to get fine-grained castings 95 per cent of the time or 90 per cent of the time. You must have them 100 per cent of the time. We believe, therefore, that it is desirable to get through some grain-refining treatment in each melting cycle when you are making production if you want consistent fine grain, and that refining treatment may be by any of these processes, such as the adding of carbon, the actual thermal process of superheating or any number of things that have been worked out by various investigators, and reported in other places.

N. TİNER (author's reply).—The suggestion made by Dr. Busk that the role of manganese may be more that of prevention of grain growth in the solid than of nucleation of grains in the liquid, is very interesting.

I made experiments with A.S.T.M. 17 and A.S.T.M. 4 alloys and found that the grain sizes of the specimens in the as-cast state confirm the measurements made after heat-treatment. The alloys heated 12 to 16 hr. at 400°C. showed no appreciable change in grain size, whereas those heated 48 to 72 hr. at 415°C. exhibited an abnormal local grain growth or "germination." No experiments are made with the manganese-free specimens, but the examination by eye of the superheated binary magnesium-aluminum alloy specimens in the as-cast state showed that they have relatively large grains on the order of 15 to 30 grains per square millimeter.

It has been shown by A. T. Peters, R. S. Busk and H. E. Elliot¹⁸ that:

1. Germination never occurs in castings that have an as-cast grain size greater than 0.005 in., or 62 grains per square millimeter.

2. A modified C alloy composition containing no manganese germinates more seriously than normal C alloy.

3. Germination does not occur until 4 to 5 hr. after all massive compound has been dissolved.

4. Germination occurs during heat-treatment by a general recrystallization of the as-cast structure, followed by the early coalescence of grains at a few spots throughout the casting and by growth of the germinant grains so formed.

In the samples prepared for superheating experiments, I did not observe any grain-size contrast that might be set up by germination. The extremely pure 8.9 per cent aluminum alloy sample mentioned in the paper was solution heat-treated at 380° to 390°C. for 14 hr. In this treatment and in other treatments, I believe the samples had just enough time for dissolving completely the massive compound. In pure magnesium-aluminum alloys superheating was found to be associated not only with manganese but also with iron. And I do not believe that Peters, Busk and Elliott mention any minimizing effect of minor iron additions on the germination tendency of the alloys.

Therefore I am of the opinion that the presence of manganese may have a minimizing effect on the germination tendency of cast alloys in the solution heat-treatment, but it also has a nucleation effect on superheated melts.

I should like to comment with respect to the question brought up by Dr. Lorig; namely, whether the melting of the alloys in graphite crucibles and the use of carbothermic magnesium did not influence also the grain refinement attributed to superheating alone.

In a recent paper, C. H. Mahoney, A. L. Tarr and P. E. LeGrand¹⁹ showed that the carbon inoculation of magnesium alloys containing aluminum exhibits a grain refining effect even though the melts have not been heated higher than 800°C., and suggested that some compound of magnesium with Al_4C_3 , or of aluminum, magnesium and carbon, may be responsible for fine-grain formation during superheating.

The alloys investigated by these authors always contained small amounts of manganese, and no information was given to show whether

¹⁹ C. H. Mahoney, A. L. Tarr and P. E. LeGrand: Factors Influencing Grain Size in Magnesium Alloys and a Carbon Inoculation Method for Grain Refinement, *Trans. A.I.M.E.* (1945) 161, 328.

magnesium-aluminum alloys could be beneficially inoculated with carbon in the absence of manganese or whether superheating effect could be observed in the complete removal of carbon. They also note the absence of any close relationship between iron content and grain size. These observations were again limited to magnesium-aluminum alloys containing small amounts of manganese and not to pure binary alloys.

It is apparent that aluminum, manganese or iron, as well as carbon, seems to be important in connection with the superheating effect and that further investigations are to be made to determine the true nature of minor constituents responsible for the effect.

In the preparation of the samples for superheating experiments, the choice of carbon crucible was mainly to control the effect of iron. Later other investigators noticed the importance of carbon in this connection, and our choice did not turn out superior. However, as Mr. Nelson pointed out, the beneficial effect of the carbon that may be picked up from the crucible is slight, particularly after using the crucible a few times, and shows only a slight tendency to lower the temperature at which superheating effects are observed.

With respect to Mr. Scrivener's question

concerning the iron content for maximum corrosion resistance and the minimum iron content for grain refining, few words can be added to Mr. Nelson's remarks.

I have pointed out that no effect of iron is noticeable on superheating cast alloys, and that the iron content of binary magnesium-aluminum alloys exhibiting superheating effect is usually above the liquid solubility limit near the freezing point. However, this is a semi-quantitative statement and no sharp tolerance limit for iron is established.

In studying the corrosion of magnesium alloys, J. D. Hanawalt, C. E. Nelson and J. A. Peloubet²⁰ note that the tolerance limit for iron is about 0.0005 per cent with 7.0 per cent aluminum and too low to be determined with 10.0 per cent aluminum. These limits do not correspond to the liquid solubility of iron near the freezing point in 9 per cent aluminum alloy at 0.005 per cent iron.

For magnesium-aluminum alloys containing small amounts of manganese, these authors find no relationship between the corrosion tolerance limit at 0.002 per cent iron and the liquid or the solid solubility limit.

²⁰ Corrosion Studies of Magnesium and Its Alloys. *Trans. A.I.M.E.* (1942) **147**, 273.

Rates of High-temperature Oxidation of Magnesium and Magnesium Alloys

BY T. E. LEONTIS* AND F. N. RHINES,† MEMBER A.I.M.E.

(Chicago Meeting, February 1946)

THE oxide scale that forms upon magnesium at elevated temperatures is non-protective in the sense that the rate of oxidation is constant and thus does not decrease with the growth of the scale as it does with other common metals. This generality was first stated by Pilling and Bedworth¹ and has been verified by Suzuki² and by Scheil.³ Pilling and Bedworth argued that the nonprotective characteristic could be predicted from the fact that magnesium oxide occupies less space than does the metal from which it springs, wherefore the scale is not expected to cover the metal so completely as to exclude all direct access to the atmosphere. Linear oxidation is thought by Scheil to be common to all cases where the reaction occurs at the oxide-metal interface.

According to Suzuki,² the product of high-temperature oxidation in the air is MgO contaminated with no more than traces of a nitride. When the metal is allowed to burn freely a fume composed of cubic crystals of MgO⁴ is given off.

This paper represents part of a thesis submitted by T. E. Leontis to the Graduate Committee of the Carnegie Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Science. Manuscript received at the office of the Institute Dec. 1, 1945. Issued as T.P. 2003 in METALS TECHNOLOGY, June 1946.

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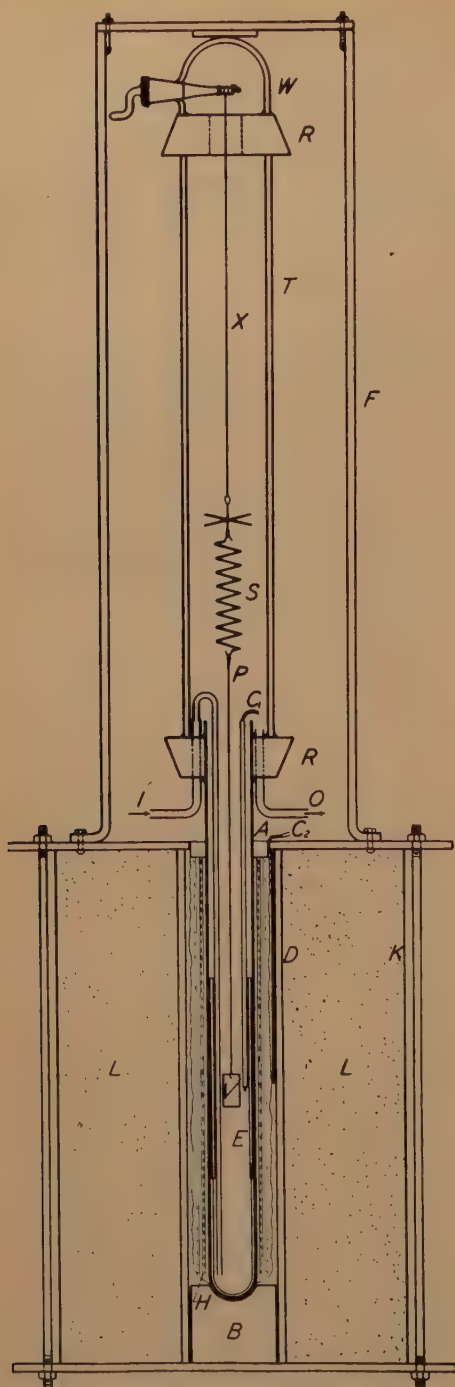
¹ References are at the end of the paper.

Delavault⁵ observed that excrescences form upon liquid magnesium and alloys in the course of oxidation. Beyond this it is known that the use of atmospheres containing small quantities of sulphur dioxide⁶ or carbon dioxide serve to retard the oxidation of solid magnesium and that beryllium⁷ and calcium⁸ minimize the oxidation of molten magnesium exposed to the air.

Many studies have been devoted to the nature and rates of "protective" oxidation, as exemplified by the cases of copper and iron, wherein the rate is characteristically parabolic. The theory of parabolic oxidation is well developed.⁹ Linear oxidation, on the other hand, has received but little attention and the theories proposed by Pilling and Bedworth and by Scheil have yet to withstand careful examination. There exists no comprehensive survey of the high-temperature oxidation of magnesium (or of any other metal that exhibits linear oxidation) over a broad range of temperature, under a variety of atmospheric conditions and covering a large group of alloys. It has been the purpose of the present investigation to provide such a survey, with the object of gaining a fuller understanding of linear oxidation, especially as applied to magnesium.

EXPERIMENTAL PROCEDURE AND RESULTS

The experimental studies undertaken were of two kinds: (1) measurement of the rate of oxidation as influenced by the



several variables mentioned above and (2) supplementary experiments designed primarily to discover what structural changes accompany the oxidation process.

Measurement of Rates of Oxidation

Throughout the present investigation the extent of oxidation was followed by a continuous measurement of the weight increase of the sample under observation, using the equipment represented diagrammatically in Fig. 1. Thus the likelihood of error resulting from spalling with temperature change was minimized. The apparatus involves no essentially new features. Calibrated silica springs* (S) have been used for weighing in certain kinds of analytical work;¹⁰ they are sensitive to ± 0.0005 grams under a total load of 0.5 grams and possess the special advantages of relative insensitivity to temperature change and linear response to loading. Positive temperature control to $\pm 0.5^\circ\text{C}$. and uniformity over a length of 5 in. was achieved by the use of a heat distributor composed of an aluminum tube E, in addition to the usual thermoelectric control system C₂. The furnace chamber A, made of Pyrex (or silica) glass, was made gastight and was provided with an inlet

* Supplied to us through the courtesy of the Bell Telephone Laboratories.

FIG. 1.—DIAGRAM OF APPARATUS.

- | | |
|--|---|
| A. Pyrex or silica furnace tube. | H. Furnace winding. |
| B. Supporting block of refractory material. | I. Gas inlet port. |
| C ₁ . Temperature-measuring thermocouple. | K. Furnace outside shell. |
| C ₂ . Controlling thermocouple. | L. Lagging. |
| D. Asbestos tube for holding lagging in place. | O. Gas outlet port. |
| E. Heat distributor, consisting of an aluminum tube. | P. Platinum suspension wire. |
| F. Steel frame for applying sealing pressure. | R. Rubber stoppers forming gastight seal. |
| | S. Calibrated silica spring. |
| | T. Pyrex tube. |
| | V. Specimen. |
| | W. Pyrex dome with sealed-in windlass. |
| | X. Winding string. |

port *I* arranged in such manner that a stream of any gas could be introduced, preheated to the furnace temperature. Gases were withdrawn (*O*) at atmospheric pressure through a drier and oil seal, or at lower pressures by means of a vacuum pump. The specimen suspension consisted of a fine platinum wire insulated from actual contact with the magnesium by means of a small alumina sleeve, which was passed through a hole in the sample *V*. In all tests the furnace conditions were adjusted before the sample was lowered into the hot zone, whereupon the recording of time and spring extension was begun at once.

TABLE I.—*Chemical Composition of Alloys Studied*

Alloy No.	Weight Per Cent by Chemical Analysis	Weight Per Cent by Spectrographic Analysis ^a
1	1.78 Al	
2	3.81 Al	(0.003 Pb)
3	7.23 Al	(0.003 Pb)
4	9.12 Al	
5	18.66 Al	
6	1.54 Zn	
7	3.28 Zn	
9	3.94 Pb	(0.14 Mn)
10	3.78 Sn	(0.010 Mn)
11	3.86 In	
12	3.94 Tl	(0.015 Mn)
13	2.38 Ga	(0.015 Mn)
14	4.18 Cd	(0.002 Pb)
15	3.83 Ag	(0.015 Mn, 0.002 Pb)
17		0.21 Si, (0.007 Fe, 0.08 Mn)
18		0.006 Fe, (0.10 Mn, 0.004 Pb)
19		0.49 Ni, (0.03 Mn, 0.004 Pb)
20		0.24 Ce, (0.32 La, 0.032 Fe, 0.04 Mn, 0.016 Pb)
21		0.03 Ca, (0.044 Mn, 0.003 Pb)
22	4.14 Mn	(0.023 Pb)
23		0.23 Cu, (0.001 Fe, 0.032 Mn)

^a Unintended elements in parentheses.

Recast sublimed magnesium analyzing 99.95 per cent Mg with no more than 0.01 Al, 0.01 Cd, 0.01 Cu, 0.001 Fe, 0.01 Mn, 0.001 Ni, 0.001 Pb, 0.01 Si or 0.01 Zn was used throughout the work. Alloys were prepared by melting 200 grams of this material in a graphite crucible under a chloride flux (Dow No. 310), adding the purest available grades of the alloying elements, and casting in a heated (500°C.) graphite mold. Analyses appear in Table I.

Sheet stock was made by hot-rolling the scalped ingots in successive reductions of 10 per cent with intermediate annealing at 350°C.

Pure magnesium and alloy samples, approximately $\frac{1}{2}$ by 1 by $\frac{1}{32}$ in., were made both from cast material and from rolled sheet stock. Although no measurable difference in the oxidation rate was found when the degree of fineness of the surface finish was changed, care was taken to standardize the surface preparation. The standard procedure followed the sequence: (1) rough grind with several grades of coarse Aloxite papers, (2) anneal in charcoal at 350°C. for 2 hr., (3) smoothing on finer Aloxite papers to $\frac{1}{2}$ or 500 grit, (4) washing with carbon tetrachloride and (5) drying between blotters. Finished samples were handled only with tongs and cotton, in order to avoid fingerprints and scratches.

Various gases and gas mixtures used during the course of this work were handled in one of several ways. Many preliminary experiments were made with air taken from the laboratory compressed-air supply and dried by passing through calcium chloride and Ascarite. For the greater part of the work, tank oxygen, tank nitrogen, and mixtures of these gases were purified by passing through calcium chloride, Ascarite, and magnesium perchlorate in that order. Sulphur dioxide and carbon dioxide were also taken from commercially supplied tanks and dried by passing through calcium chloride and magnesium perchlorate. Gas mixtures of specific composition were prepared by manipulation of the tank valves until the desired analysis was attained. The gas components were first introduced into a large carboy, and to ensure thorough mixing they were transferred by means of an oil pump to a second carboy, from which the mixture was delivered to the furnace under a slight pressure developed in the carboy. Samples were drawn periodically

from the second carboy for analysis by means of an Orsat apparatus. In general a stream of about 40 c.c. per minute was employed.

among the slopes (k) found in duplicate experiments were observed. In order to show the range of variation, the curves of maximum and minimum slope found at

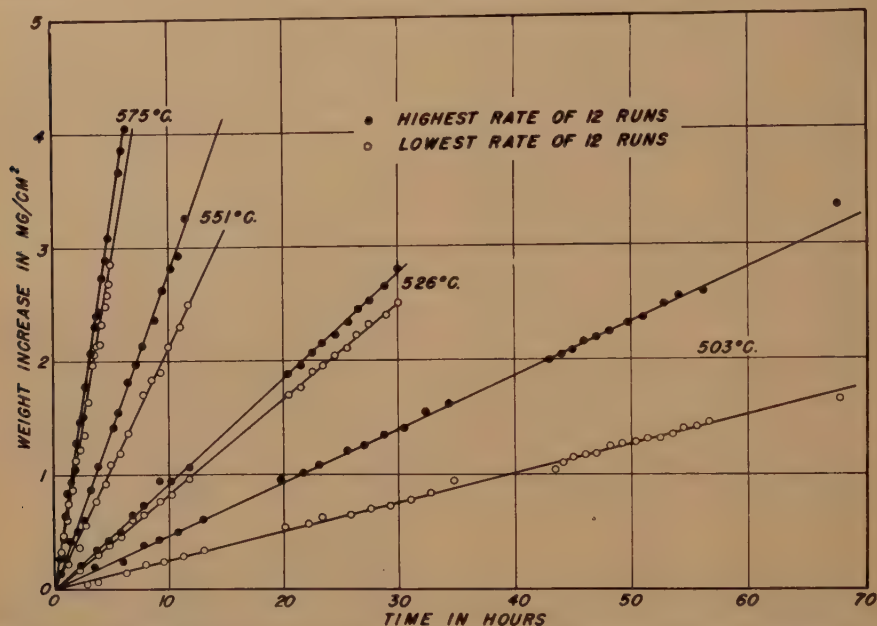


FIG. 2.—OXIDATION OF ROLLED PURE MAGNESIUM IN PURE OXYGEN AT FOUR TEMPERATURES.

Results of Rate Measurement on Pure Magnesium

The findings about to be described are based upon the observation of the oxidation of more than 150 samples of pure magnesium and more than 250 alloy samples. Typical curves of the increase of weight with time, for pure wrought magnesium in oxygen at atmospheric pressure, are presented in Fig. 2. Attention is directed to the precise linear form throughout the lengths of these plots. The curves conform to the expression:

$$k = \frac{W}{t}$$

where k is the rate constant in mg. per sq. cm. per hr., W is the cumulative weight in mg. per sq. cm. and t is the time in hours. Twelve check samples were oxidized at each temperature and some variation

each temperature are included in Fig. 2. In general, most of the curves at a given temperature lie close to the curve representing the average rate. It is noteworthy that after long oxidation at 575°C. the rate sometimes increased (Fig. 3) but on its new slope the plot continued to be linear.

When the logarithm of the average slope k at each temperature is plotted as a function of the reciprocal of the absolute temperature of oxidation a linear relationship is again found (Fig. 4). Here:

$$k = Ae^{-E/RT}$$

where A is the action constant, E the energy of activation in small calories for this process, R the gas constant and T the absolute temperature. The energy of activation E read from the slope of the latter

curve is 50,500 cal. and A has a value of 6.2×10^{12} mg. per sq. cm. per hour.

Oxidized in the air, either cast or rolled magnesium follows a somewhat different

and Bedworth report a rate of 0.52 mg. per sq. cm. per hr. for oxidation in air at 500°C ., corresponding to the presently reported rate of 0.13 mg. per sq. cm. per

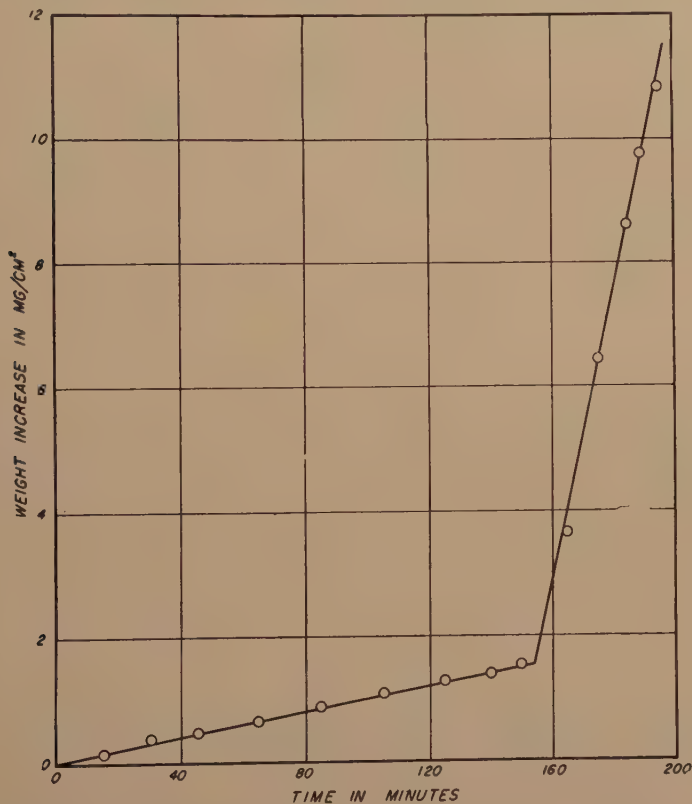


FIG. 3.—OXIDATION OF ROLLED PURE MAGNESIUM AT 575°C . IN PURE OXYGEN, SHOWING ABRUPT INCREASE IN RATE OF OXIDATION.

course (Fig. 5). The curve is linear with two limbs and there is an induction period during which very little, if any, weight increase is detected. When the initial and final rates (first and second limb) read from a number of curves are averaged to obtain a plot of the logarithm of the rate versus the reciprocal of the absolute temperature, a linear relationship appears as before (Fig. 4) and the energy of activation E remains 50,500 cal. in both cases; A for the initial rate is 2.7×10^{13} mg. per sq. cm. per hr. and for the final rate 3.6×10^{13} mg. per sq. cm. per hr. Pilling

hr. at the same temperature, while Suzuki obtained a rate of 0.97 mg. per sq. cm. per hr. at 560°C ., corresponding to the present 1.38 mg. per sq. cm. per hr. These constitute fair agreement, considering the wide differences among individual determinations found by all investigators.

The wrought magnesium used in these studies possesses a preferred orientation with the basal plane of the hexagonal crystal in the rolling plane of the sheet. A group of samples was prepared with the broad faces of some in the rolling plane and the broad faces of others perpendicular

to the rolling plane and parallel to the direction of rolling. The latter exhibited a slightly faster rate of oxidation (Table 2). In all other experiments the samples were

taken with their broad faces parallel to the rolling plane, corresponding to the slower rate. Lest an error had been introduced into

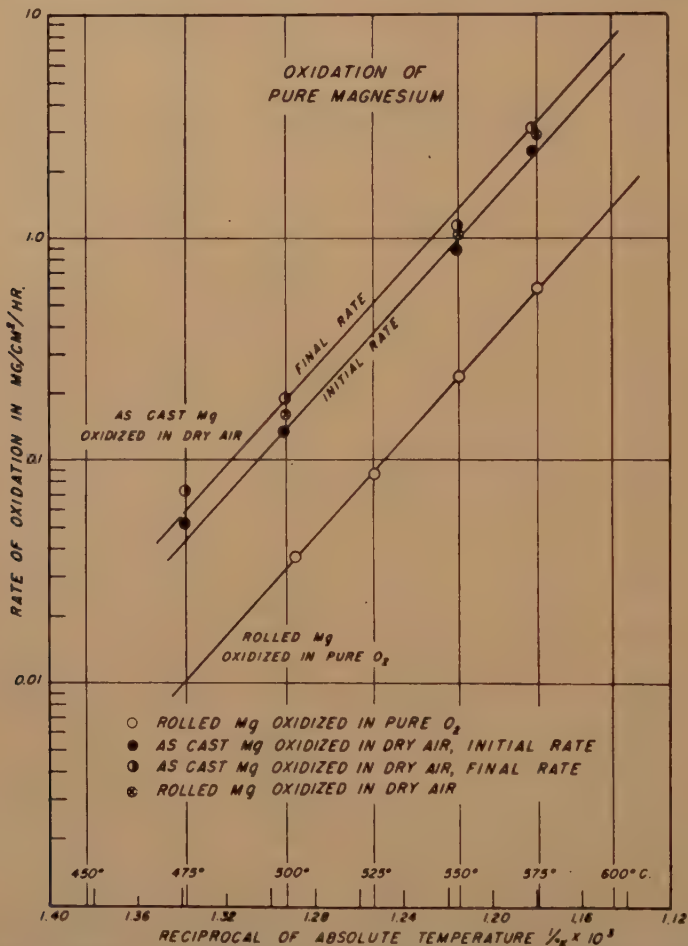


FIG. 4.—EFFECT OF TEMPERATURE ON OXIDATION RATE OF PURE MAGNESIUM.

TABLE 2.—Effect of Crystal Orientation on Rate of Oxidation of Pure Magnesium at 550°C.

Orientation of Surface with Respect to Basal Plane	Range of Oxidation Rate, Mg. per Sq. Cm. per Hr.	Average Oxidation Rate, Mg. per Sq. Cm. per Hr.
Parallel.....	0.132-0.152	0.141
Perpendicular.....	0.153-0.190	0.184

the measurements through the loss of magnesium oxide as smoke, some samples were oxidized completely and the weight increase was compared with that calculated upon the assumption that all of the metal was converted to magnesium oxide (MgO). The measured weight increase was very slightly greater than the calculated figure, from which it is concluded that no magnesium oxide has been lost

in this way. To avoid the loss of the oxide when its supporting backing of metal had been consumed, it was necessary to conduct

rates from these data it was found that good agreement with cases in which no spalling had occurred could be obtained

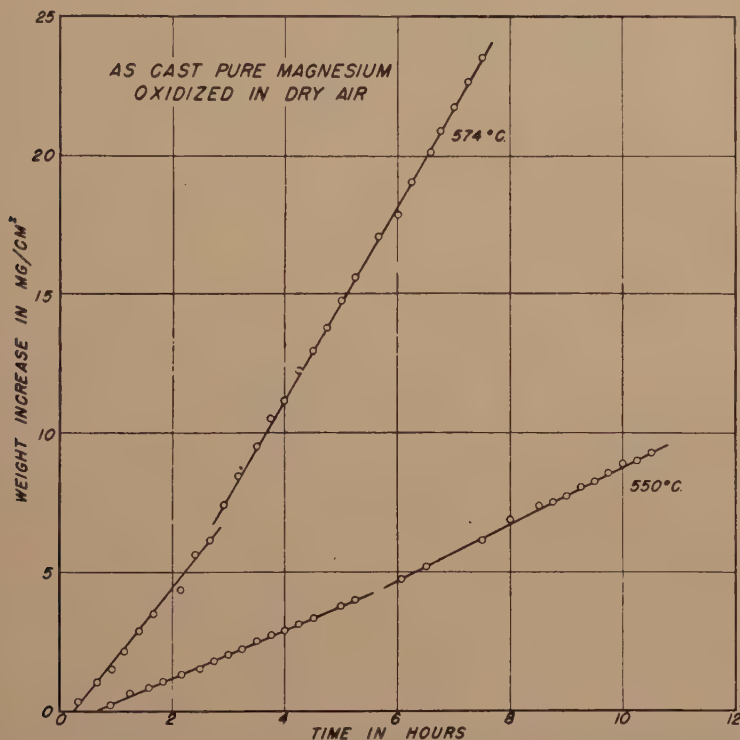


FIG. 5.—OXIDATION OF CAST PURE MAGNESIUM IN DRY AIR AT TWO TEMPERATURES. Time interval between origin and beginning of curve is an induction period.

this test by oxidizing the specimen in a platinum boat in an atmosphere of oxygen. The absence of any deposit upon the furnace walls as a result of oxidizing pure magnesium, except when the sample had ignited, is taken as further evidence that no oxide was lost in the form of smoke.

In a few of the experiments spalling occurred, usually as the result of mechanical shock. This resulted in a sudden decrease in weight, after which the regular increase in weight was resumed at the former rate. The resulting oxidation curve was made up of two or more sections having the same slope but vertically displaced from each other. In calculating the

rates from these data it was found that good agreement with cases in which no spalling had occurred could be obtained

Results of Rate Measurements on Alloys

The addition of aluminum to magnesium increases the rate of oxidation progressively, up to the limit of the solid solubility of aluminum in magnesium (Fig. 6). Simple linear oxidation is again found (Fig. 7) except in the alloys with larger aluminum contents, where the period of linear oxidation is preceded by an incubation period during which the rate gradually increases to that of linear oxidation. The temperature variation of the rate for a series of magnesium-aluminum alloys is

given in Fig. 8. Here it will be seen that the slope E changes with composition (Table 3), falling to a minimum in the

Much the same behavior is found with small zinc additions (Figs. 9 and 10) except that the energy of activation E

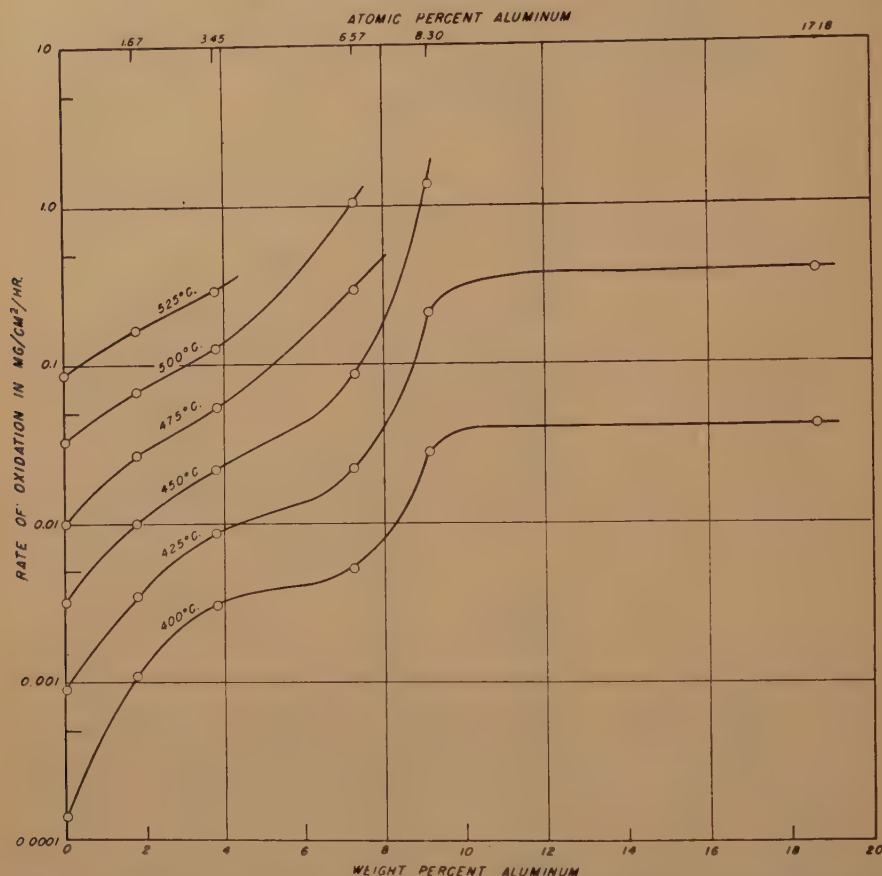


FIG. 6.—CHANGE OF OXIDATION RATE WITH ALUMINUM CONTENT AT SIX TEMPERATURES.

alloy with 3.81 per cent Al and then rising above the value for pure magnesium.

TABLE 3.—Energies of Activation and Action Constants for Rate of Oxidation of Magnesium-aluminum Alloys

Aluminum Content, Wt. Per Cent	Energy of Activation E , Cal. per Mol	Action Constant A , Mg. per Sq. Cm. per Hr.
1.78	42,700	9.0×10^{10}
3.81	38,600	1.1×10^{10}
7.23	54,700	2.7×10^{15}
9.12	74,500	4.0×10^{22}

remains 50,000 cal. Larger zinc additions (3.28 per cent Zn) lead to irregular behavior, which, it is believed, result from a loss of zinc by vaporization, for a residue was found on the furnace wall.

Similar measurements on 14 other binary alloys exposed to oxygen at atmospheric pressure are recorded in Figs. 11, 12, and 13. It is noteworthy: (1) that nickel and copper are, of all the alloying agents examined, the most effective in accelerating oxidation; (2) that the elements Fe, Ag, In, Pb, Mn, Ca, Si and Cd have but a

minor influence upon the rate; (3) that Sn and Ga are most effective in lowering the energy of activation, which means that they increase the rate more at low tem-

materially reduced the rate was Ce + La. Most of the measurements in this group rest upon small numbers of tests and the departure from regular variation with

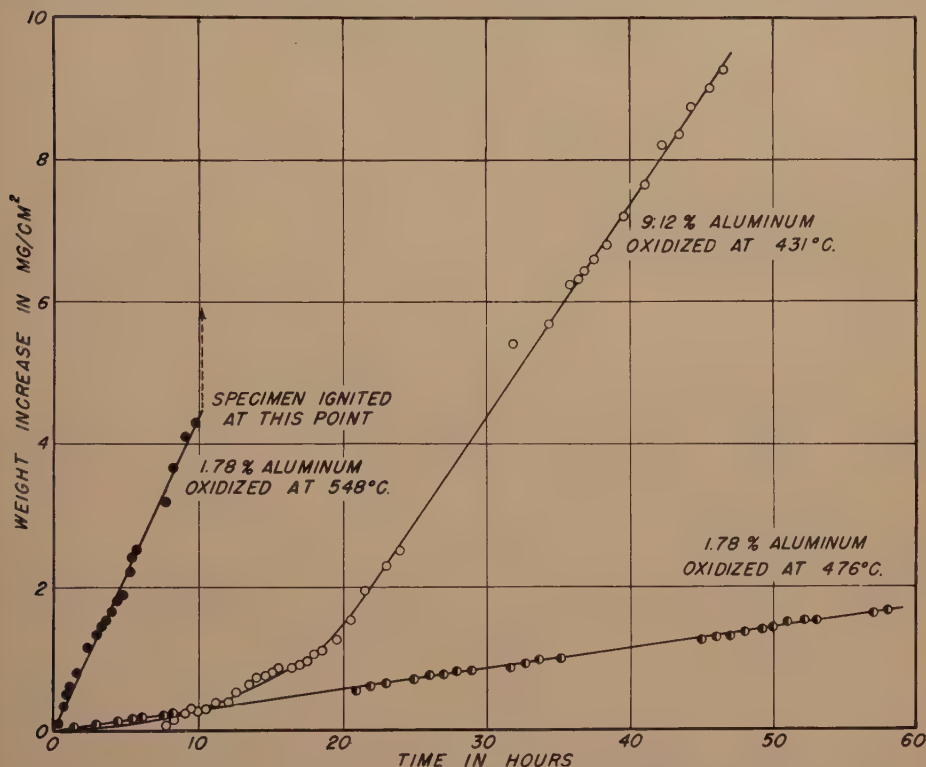


FIG. 7.—TYPICAL OXIDATION CURVES FOR MAGNESIUM-ALUMINUM ALLOYS.

peratures than at high temperatures; and (4) that the only combination studied that

temperature may, therefore, be without real significance. Values of the energies of activation (Table 4) are, accordingly, less to be trusted than those for the pure magnesium and the magnesium-aluminum alloys.

TABLE 4.—Energies of Activation and Action Constants for Rates of Oxidation of Various Magnesium Alloys

Composition, Wt. Per Cent	Energy of Activation E , Cal. per Mol	Action Constant A , Mg. per Sq. Cm. per Hr.
1.54 Zn	50,000	1.1×10^{13}
3.28 Zn	31,500	1.0×10^8
3.83 Ag	52,600	3.9×10^{13}
3.78 Sn	31,600	1.2×10^8
3.86 In	46,600	8.1×10^{11}
2.38 Ga	30,700	7.6×10^7
4.18 Cd	50,500	6.2×10^{12}
3.94 Ti	50,500	6.2×10^{12}
3.94 Pb	51,600	2.7×10^{13}
0.49 Ni	42,000	3.5×10^{11}
0.23 Cu	44,800	2.4×10^{12}
0.006 Fe	50,500	4.5×10^{12}

Results of Rate Measurements in Various Gases and in Oxygen at Reduced Pressures

In order to obtain a brief survey of the effects of various gases and gas mixtures at atmospheric pressure upon pure magnesium, a series of experiments was made at 550°C. (Table 5). The presence of water vapor greatly accelerates oxidation, while additions of sulphur dioxide and carbon

dioxide virtually suppress oxidation. Dilution of oxygen with various amounts of nitrogen gave irregular results.

temperatures and E. A. Gulbransen* kindly consented to measure some rates on his more sensitive vacuum microbalance,

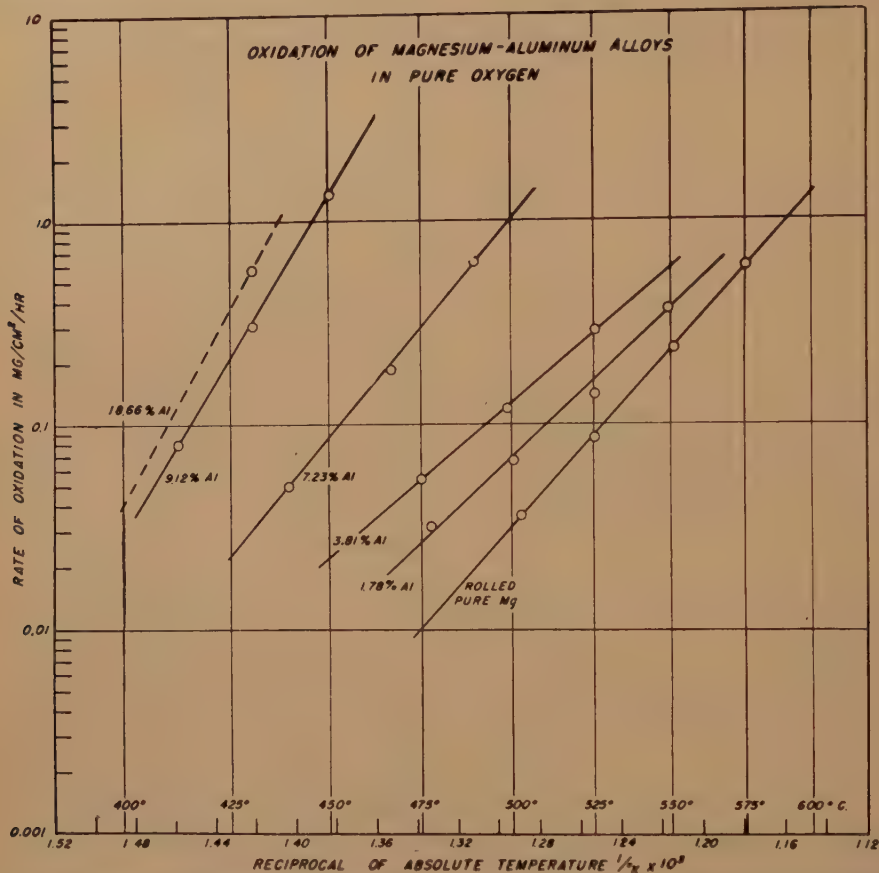


FIG. 8.—EFFECT OF TEMPERATURE UPON OXIDATION RATES OF MAGNESIUM-ALUMINUM ALLOYS.

The apparatus employed in this research proved to be too insensitive for rate measurements at low pressures and

using our pure magnesium samples. This work developed into a separate research, the results of which have already been published,¹¹ but which we quote in part with permission. A summary of the rates found by oxidizing rolled magnesium samples at reduced pressures of pure oxygen appears in Table 6. The room-temperature film was not removed before oxidation. These data show that the rate of protective oxidation decreases with

TABLE 5.—Rate of Oxidation of Pure Magnesium at 550°C. in Various Gases at Atmospheric Pressure

GAS	RATE OF OXIDATION, MG. PER SQ. CM. PER HR.
Pure O ₂	0.24
O ₂ saturated with H ₂ O at 28°C.....	0.61
Pure CO ₂	Negligible
Pure SO ₂	Negligible
O ₂ + 5% SO ₂	Negligible
O ₂ + 11% CO ₂	Negligible
1% O ₂ + 99% N ₂	0.026
50% O ₂ + 50% N ₂	0.059

* Westinghouse Electric & Manufacturing Company, Research Laboratories.

decreasing oxygen pressure but that the change in rate is in no way proportional to the change in oxygen pressure. It was

found that the rate decreases with time (protective oxidation) up to and including 450°C. and is linear at 475°C. and above.

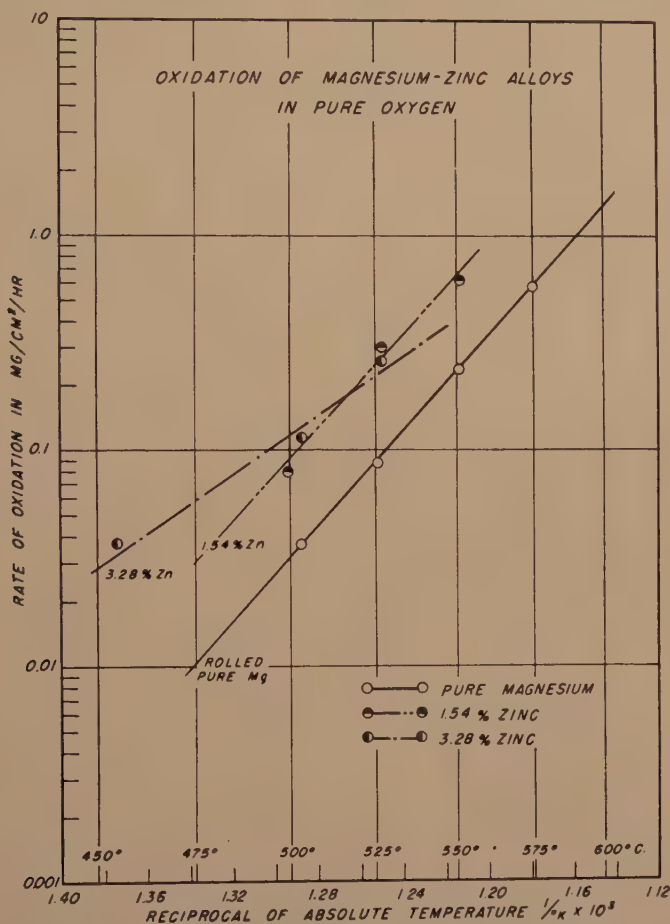


FIG. 9.—EFFECT OF TEMPERATURE UPON OXIDATION RATES OF MAGNESIUM-ZINC ALLOYS.

TABLE 6.—Effect of Oxygen Pressure on Rate of Oxidation of Pure Magnesium (Gulbransen¹¹)

Temperature, Deg. C.	Oxygen Pressure, Mm. Hg	Maximum Oxidation Rate, Mg. per Sq. Cm. per Hr.	Type of Scale
500	200	0.072	Nonprotective
475	200	0.00684	Nonprotective
475	2	0.00288	Protective
450	200	0.00198	Protective
450	20	0.00150	Protective
450	2	0.00078	Protective
425	200	0.00060	Protective
400	200	0.00060	Protective
400	2	0.00054	Protective

Before and after each experiment, the specimen was held for some time at temperature in a high vacuum, so that the rate of vaporization of the magnesium could be observed. From this it was learned that the protective oxide formed at 450°C. or below tends to block the evaporation of magnesium, while the loose high-temperature oxide permits evaporation to occur at a rate faster than that found at the beginning of the experiment.

Other Observations Concerning Rate of Oxidation

Beside the systematic observations presented, some incidental observations deserve mention. Sauereisen Cement No. 31

shortly by actual combustion, interferes with measurements at 600°C. At 575°C. this effect was sometimes encountered just before the sample was completely oxidized; for example, see Fig. 7.

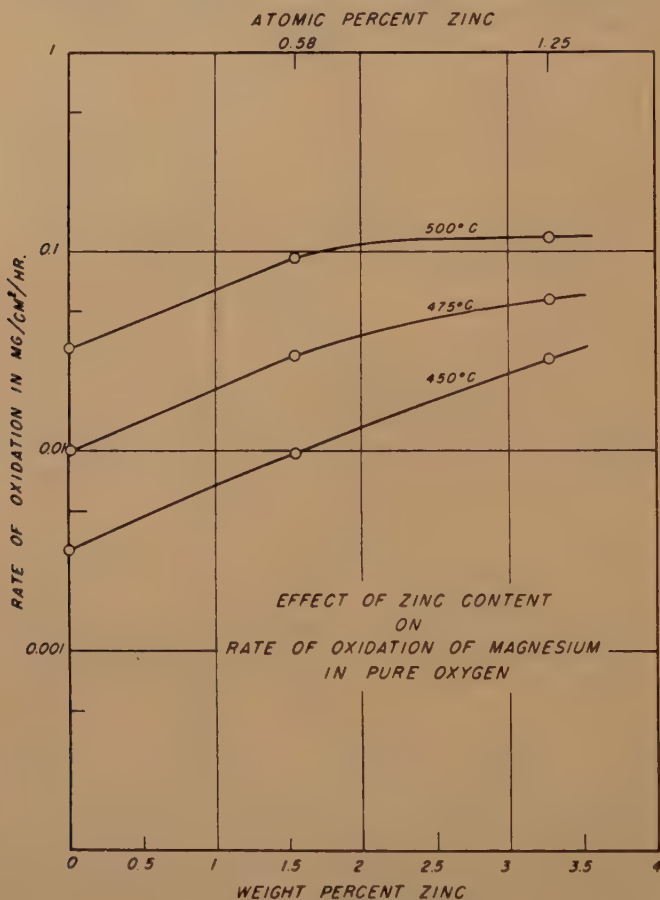


FIG. 10.—CHANGE OF OXIDATION RATE WITH ZINC CONTENT.

was used at one time in the assembly of one of the furnaces. Oxidation in this case was largely suppressed and when it did occur it was limited to a relatively small number of patches on the sample. Normal behavior was resumed when the cement was removed. The Constable effect (a spontaneous rise in the temperature of the sample as a result of heat evolved by the oxidation process), followed

STUDY OF STRUCTURE

The nature of the products of oxidation has been studied through the application of macroscopic, optical and electron microscopic, X-ray and electron diffraction and spectrographic methods with the following results.

Macrostructure

1. The oxide grows directly outward from each surface, leaving the corners

vacant; indicating that the reaction takes place at the metal-oxide interface (Fig. 14). Surface markings present upon the original metal surface are retained upon the outer oxide surface (Fig. 15).

3. On specimens oxidized only long enough to obtain one branch on the oxidation curve, only the outside, dense layer formed. This oxide usually spalled off the metal surface when the specimen

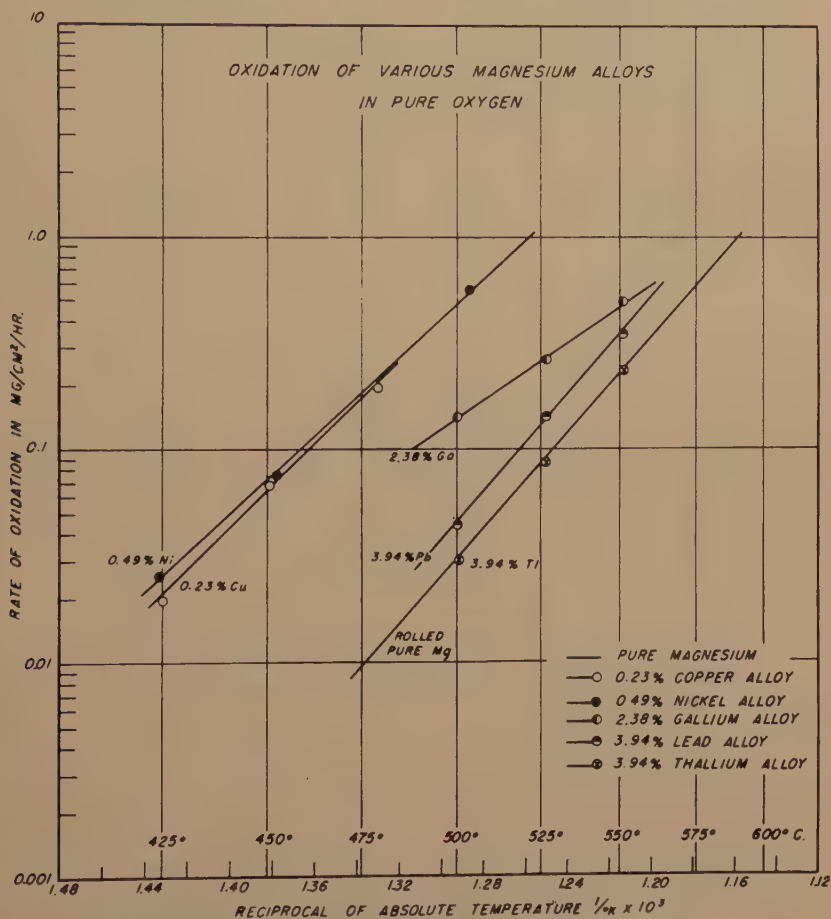


FIG. 11.—EFFECT OF TEMPERATURE UPON OXIDATION RATES OF VARIOUS MAGNESIUM ALLOYS.

2. Where oxidation has proceeded long enough to form two branches of different slope on the oxidation curve, the oxide consists of two distinct layers; an outer layer perhaps 0.001 in., thick, which is very dense and brittle, and an inner layer composed of a relatively loose, powdery mass, which usually appears stratified and is not as white as the outer dense layer (Fig. 16).

was removed from the furnace. At low oxidation temperatures (500°C.) the oxide was not as dense as that formed at the higher temperature, probably because it had not acquired the thickness of the latter.

4. The metal surface becomes progressively less smooth and is darkened as oxidation proceeds. Irregularities in the extent of oxidation from grain to grain

were observed and a certain amount of pitting also took place. In the early stages of oxidation the surface assumes a brownish color. On more extensively oxidized speci-

of the material in bulk form. It is noteworthy that this black material persists on the metal surface throughout the oxidation process, and forms the core of

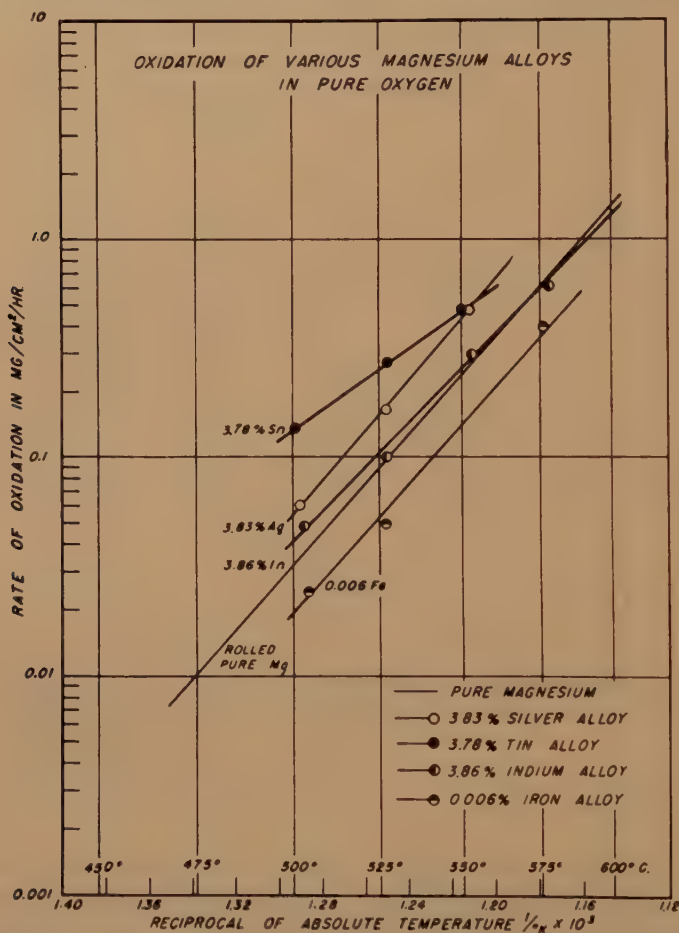


FIG. 12.—EFFECT OF TEMPERATURE UPON OXIDATION RATES OF VARIOUS MAGNESIUM ALLOYS.

mens parallel striations were observed within each grain. These were found to be traces of the basal plane. Also, a black crustaceous material was found next to the metal surface on such specimens. X-ray and electron diffraction analysis have shown this to be MgO . The color may be caused by a deficiency in either magnesium or oxygen atoms; this can be ascertained only by conductivity measurements

the oxide when the metal has been completely oxidized.

5. The same characteristics prevail in the relation between the oxide structure and the oxidation curves of alloys. In addition, there were obtained oxidation curves in which the initial part was curvilinear and the rate increased to that of the linear branch of the curve. Under such conditions, the oxide again consisted

of an outer dense layer and an inner loose mass. This inner layer is usually much looser than the corresponding part of the oxide on pure magnesium.

6. In addition to the darkening of a

7. In a general way, the presence of alloying elements appears to cause the inner layer of the oxide to assume a looser texture, with less tendency toward stratification than in pure magnesium.

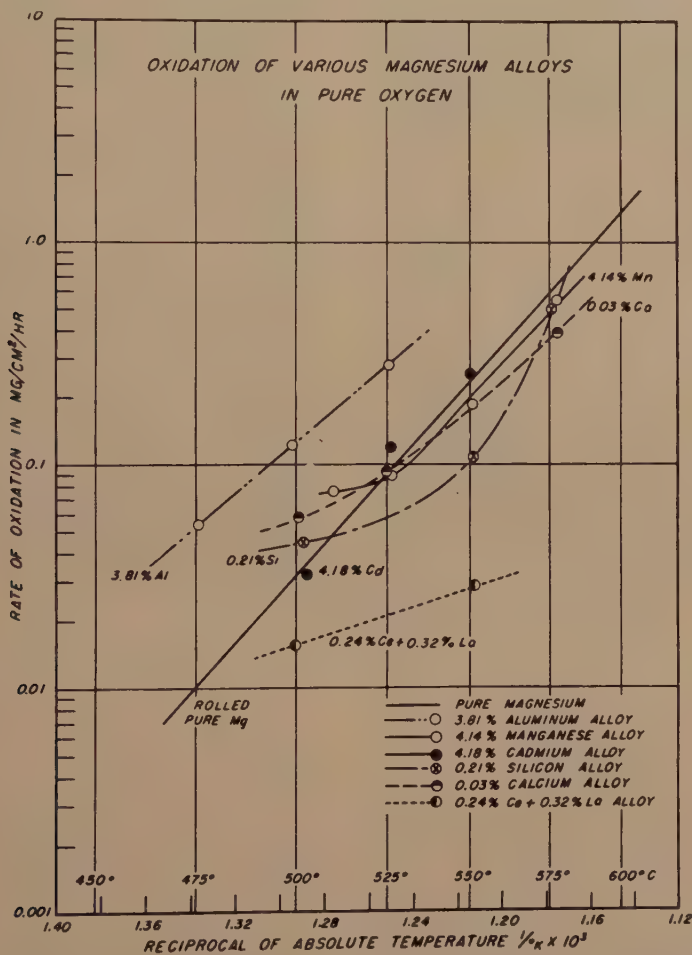


FIG. 13.—EFFECT OF TEMPERATURE UPON OXIDATION RATES OF VARIOUS MAGNESIUM ALLOYS.

zone next to the metal, the major part of the oxide may be colored by the presence of alloying constituents. Aluminum and silver produce gray tints more or less in proportion to their concentration in the alloy. Manganese and copper color the oxide tan; nickel, pink; cerium, orange; and tin accentuates the whiteness of the oxide.

8. Where surface cracks were present initially in rolled samples, oxidation started early at the crack and tended to remain localized (Fig. 17).

Microstructure

1. Electron microscope pictures of disintegrated loose scales from magnesium and its alloys showed the presence of

cubes in all samples examined (Figs. 18 and 19). In addition, there were sometimes unresolved masses, which probably consist of undispersed aggregates of particles.



FIG. 14.—OXIDIZED SPECIMEN OF PURE MAGNESIUM, SHOWING SEPARATION OF OXIDE SCALE INTO LAYERS. $\times 2$.

film intact. Optical examination revealed no structure in this film, which was virtually transparent. An electron microscope picture (Fig. 22) is thought to reveal no

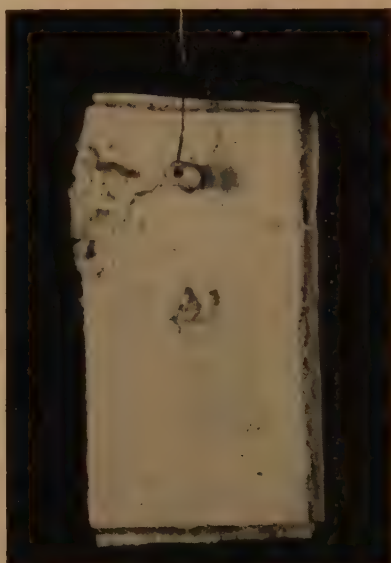


FIG. 15.—OXIDIZED SPECIMEN OF PURE MAGNESIUM, SHOWING OUTWARD GROWTH OF SCALE. $\times 3$.

2. The cube size appeared to decrease with rising temperature and with alloying, but there was always a wide variation in size within any one sample.

3. Some large lozenge-shaped particles were found in the oxide of the magnesium-lead alloy (Fig. 19b); prismatic particles appeared in the oxide of the cerium-containing alloy (Figs. 19e and f).

4. The optical microscope revealed the presence of small quantities of second phases in the oxides formed upon alloys with nickel, gallium and manganese (Figs. 20 and 21).

5. No structural changes within the metal itself except those usually associated with equivalent heat-treatments were found in any specimen.

6. Some samples of pure magnesium were completely sublimed in a high vacuum, leaving the thin room-temperature

details of structure; the markings shown are probably caused by the surface contours of the film (scratches in the original metal surface) and by the presence of nonvolatile residues, which can be seen by optical methods to be clinging to the film in some places. Holes if present would appear as white areas.

Crystal Structure

1. Lines of the MgO pattern were found in all samples.

2. In the scale formed upon the high-aluminum alloys additional reflections appear. These have been identified as lines of the spinel ($\text{MgO} \cdot \text{Al}_2\text{O}_3$) pattern.

3. An electron-diffraction examination of the very thin room-temperature film initially present on pure magnesium separated by sublimation showed it to be MgO . Such films are usually found to be



FIG. 16.—MACROSTRUCTURE OF OXIDE LAYERS. DENSER OUTSIDE LAYER INDICATED BY ARROWS.
X 23.

$\text{Mg}(\text{OH})_2$ when examined in situ at room temperature. This experiment appears to show that the room-temperature film is converted to MgO at the temperature at which the oxidation rates were measured.

4. The cellular scale is shown by X-ray diffraction to be very fine grained, with a random orientation.

Chemical Composition of Scale

A spectrographic comparison between the compositions of the oxide and of the parent metal is shown in Table 7. The actual percentages of the components were not determined because of a lack of suitable standards. The oxide retains the alloying element in all cases. If there is an error in these analyses it is probably in

the direction of underestimating the amount of alloying element in the oxide,

TABLE 7.—*Spectrographic Analyses of Oxides Formed upon Various Magnesium Alloys*

Alloy No.	Element in Alloy, Wt. Per Cent	Ratio of Concentration in Alloy and in Oxide
I	1.78 Al	2
2	3.81 Al	1
3	7.23 Al	1
4	9.12 Al	1
6	1.54 Zn	5
7	3.28 Zn	10
10	3.78 Sn	3
11	3.86 In	5
14	4.18 Cd	10
15	3.83 Ag	5
17	0.21 Si	1
19	0.49 Ni	2
20	{ 0.24 Ce	0.5
	{ 0.32 La	0.5
22	4.14 Mn	1

because the color of the scales suggested that the impurities were lodged mainly near the metal surface while the analytical samples were more representative of the

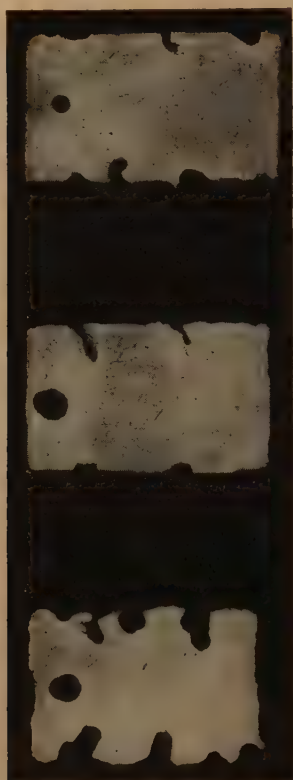


FIG. 17.—SPECIMEN SHOWING PREFERENTIAL OXIDATION ALONG EDGE CRACKS. ABOUT $\times 1\frac{1}{2}$.

outer zones of the oxide. The very low zinc and cadmium contents of the oxides formed upon alloys containing these metals are not surprising in view of the probable loss of oxide fume from these samples as cited previously.

DISCUSSION OF RESULTS

It has now been demonstrated that magnesium oxidizes in at least three distinct ways under various conditions; namely: (1) by the growth of a *protective film* at relatively low temperatures in air and perhaps also at higher temperatures

in the early stages of oxidation and especially in the presence of certain "protective" gases, (2) by the formation of a porous *nonprotective scale*, often composed of cubes of MgO , particularly at the higher temperatures and (3) by combustion with a flame at temperatures approaching and exceeding the melting point, to form a *fume* of MgO cubes. The mechanisms of oxidation proposed by Pilling and Bedworth¹ and by Scheil³ attempt to explain only the second mode of oxidation, and while they correctly predict a linear rate, they fail to define the process controlling the magnitude of the rate. Thus, a more detailed theory is required to explain the oxidation behavior of magnesium; such a theory may well include the earlier theories as integral parts of its plan.

Since magnesium burns with a flame, it is apparent that this reaction must take place in the vapor phase, where magnesium gas and oxygen meet; the possibility that the reaction could occur at the surface of the metal, where the products of reaction would be released as incandescent MgO gas, need hardly be considered because of the very low vapor pressure of MgO . The perfection of the MgO cubes that make up the fume is strongly suggestive of their growth in space where impinging surfaces cannot modify their natural idiomorphic form. Magnesium has a relatively high vapor pressure, as demonstrated by Coleman and Egerton¹² (Fig. 23), and boils at a little above $1100^{\circ}C$. at one atmosphere pressure; this temperature obviously is exceeded in the magnesium flame. Thus it may be assumed with some confidence that magnesium vapor, produced in the high temperature of the flame, burns upon meeting oxygen gas at some distance from the metal surface, producing MgO , which quickly precipitates in the form of a fume of MgO cubes. Some of the fume settles on the metal and on other near-by surfaces, giving the appearance of a loose scale formation. The rate-controlling factors are



FIG. 18.—ELECTRON MICROGRAPHS OF OXIDES FORMED ON PURE MAGNESIUM AND MAGNESIUM ALLOYS.

Original magnifications 20,000; reduced approximately one third in reproduction.

- a. Oxide from pure magnesium oxidized at 503°C.
- b. Oxide from pure magnesium oxidized at 503°C.
- c. Oxide from pure magnesium oxidized at 575°C.
- d. Oxide from alloy of Mg and 7.23 per cent Al oxidized at 490°C.
- e. Oxide from alloy of Mg and 1.54 per cent Zn oxidized at 551°C.
- f. Oxide from alloy of Mg and 3.83 per cent Ag oxidized at 502°C.

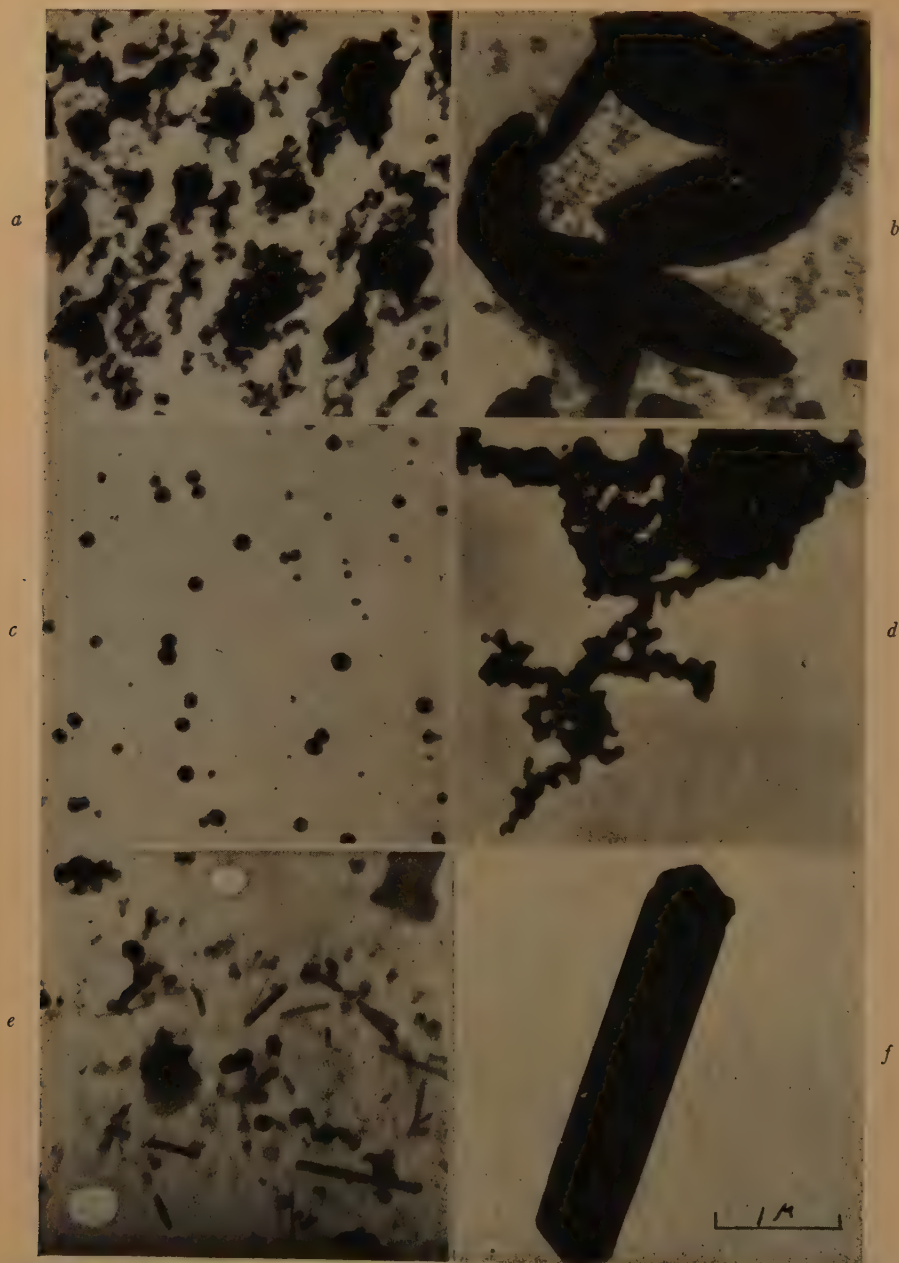


FIG. 19.—ELECTRON MICROGRAPHS OF OXIDES FORMED ON MAGNESIUM ALLOYS OXIDIZED AT 501°C .
Original magnifications 20,000; reduced approximately one third in reproduction.

a. 3.94 per cent Pb.

b. 3.94 per cent Pb.

c. 3.78 per cent Sn.

d. 2.38 per cent Ga.

e. 0.24 Ce + 0.32 La.

f. 0.24 Ce + 0.32 La.

probably highly complicated, inasmuch as they must include all conditions that can influence the concentration and dissipation of heat as well as the supply of oxygen;

Gulbransen's¹¹ observation of a nearly parabolic rate of oxidation of magnesium at low temperatures may, accordingly, be taken as evidence that normal protective



FIG. 20.—TWO-PHASE STRUCTURE OF OXIDE FORMED UPON ALLOY OF MAGNESIUM AND 0.49 PER CENT NICKEL $\times 23$.

presently available data are too fragmentary to warrant an attempt to calculate the rate of combustion.

As a result of extensive studies upon the oxidation behavior of such metals as copper,^{1,14} iron^{1,15} and nickel,^{1,16} the general theory of protective oxidation is well developed. The rate, which diminishes approximately parabolically with time, is controlled by the rate of diffusion of one of the reactants through the resulting scale layer; as the scale grows in thickness the path of diffusion increases, while the concentration of the reactants remains constant at the surface and hence the rate of delivery of the reactants decreases.

oxidation is occurring. It may be presumed that the rate of low-temperature (and initial) oxidation is controlled by the rate of diffusion of one of the reactants (probably magnesium) through a coherent film of MgO .

According to Pilling and Bedworth, magnesium should not exhibit protective (parabolic) oxidation, because the volume of the oxide is less than that of the metal consumed and a coherent scale layer should not form. The evidence at hand indicates, however, that very thin coherent films of MgO can and do form upon the metal. Low-temperature films removed by the evaporation of the metal exhibit no

system of discontinuities when viewed with the electron microscope. Gulbransen found that some low-temperature films prevent the sublimation of magnesium in vacuum, while others permit sublimation in varying

reaches some more or less critical dimension, spontaneous and systematic rupturing will occur.

This view of protective oxidation is easily reconciled with the action of the

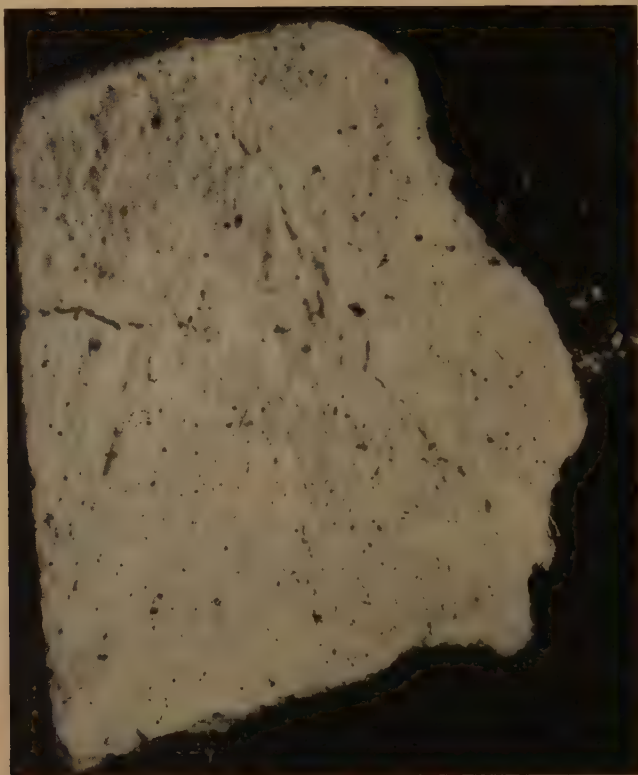


FIG. 21.—TWO-PHASE STRUCTURE OF OXIDE FORMED UPON ALLOY OF MAGNESIUM AND 4.14 PER CENT MANGANESE. $\times 23$.

degrees, indicating that no systematic rupturing of the film occurs at small thicknesses. Perhaps the explanation lies in the inherent strength of thin MgO films, which is evident in the relative ease with which they can be handled. It may be presumed that, when the film is so thin that tensile stresses are operating in an essentially two-dimensional system, the oxide can withstand the tensile stress necessary to adapt it to the dimensions of the metal; it will be necessary, presently, to add the corollary that, when the film thickness

“protective” gas atmospheres and alloying agents and, in addition, it provides an explanation of the induction period that precedes nonprotective oxidation under a variety of conditions. When moisture is present, there forms a very protective film composed largely of $\text{Mg}(\text{OH})_2$ (density 2.38), which has a volume ratio with respect to the metal (density 1.74) that is much more favorable to coherent film formation than is that of MgO (density 3.65). Similarly, sulphur dioxide, which is highly protective to magnesium and is

thought to form MgSO_4 (density 2.66), should produce a more voluminous and, therefore, a more stable coherent film. Alloying elements, such as aluminum,

critical thickness, the exact value of which will depend upon the temperature, the surface contour of the metal and the composition of the film, it is proposed that

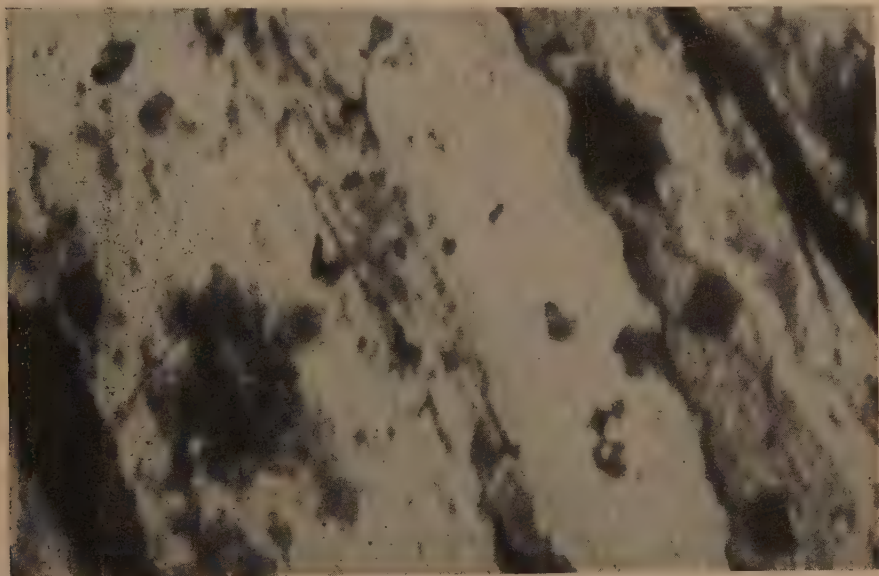


FIG. 22.—TRANSMISSION ELECTRON MICROGRAPH OF ROOM-TEMPERATURE OXIDE FILM REMOVED FROM MAGNESIUM BY SUBLIMING THE METAL IN VACUUM AT 500°C . $\times 20,000$.
Holes if present, would have appeared clear white.

copper, nickel and so on, form more voluminous oxides, and when present as such in the MgO film might be expected to increase its protective characteristic. Apparently this is true, because such alloying additions to magnesium all give rise to induction periods preceding rapid nonprotective oxidation, indicating that they tend to stabilize the protective film. The observation that the rate during the induction period does not diminish parabolically, but tends to rise continuously to the high rate of linear oxidation, need not be disturbing, because it has also been observed that nonprotective oxidation starts preferentially at edges, corners and imperfections, spreading thence over the entire surface, so that a gradual transition from protective to nonprotective oxidation is to be expected.

When the protective film reaches some

tensile ruptures appear spontaneously, admitting oxygen gas through the film and thereby accelerating oxidation. The nonprotective (linear) oxidation that follows is believed by Pilling and Bedworth and by Scheil to occur by reaction at the metal surface. A more or less porous scale grows by the deposition of new oxide at the interface between the metal and the scale.

Since the rate of nonprotective oxidation is insensitive to the thickness of the scale, it appears that the rate of delivery of oxygen to the reaction zone is not important; i.e., an excess of oxygen is present at all times. It seems most probable, therefore, that the rate of linear oxidation is controlled by the rate of the reaction of oxygen with magnesium under conditions of constant supply. If the order of the reaction can be identified, this should

serve as a guide to the mechanism of the reaction. Linear reaction is in itself proof of zero-order reaction, which has the additional characteristic that it is insensi-

by us at one atmosphere pressure; Gulbransen's data show that at 475°C. a hundredfold decrease in oxygen pressure results in only a 2.3-fold decrease in the

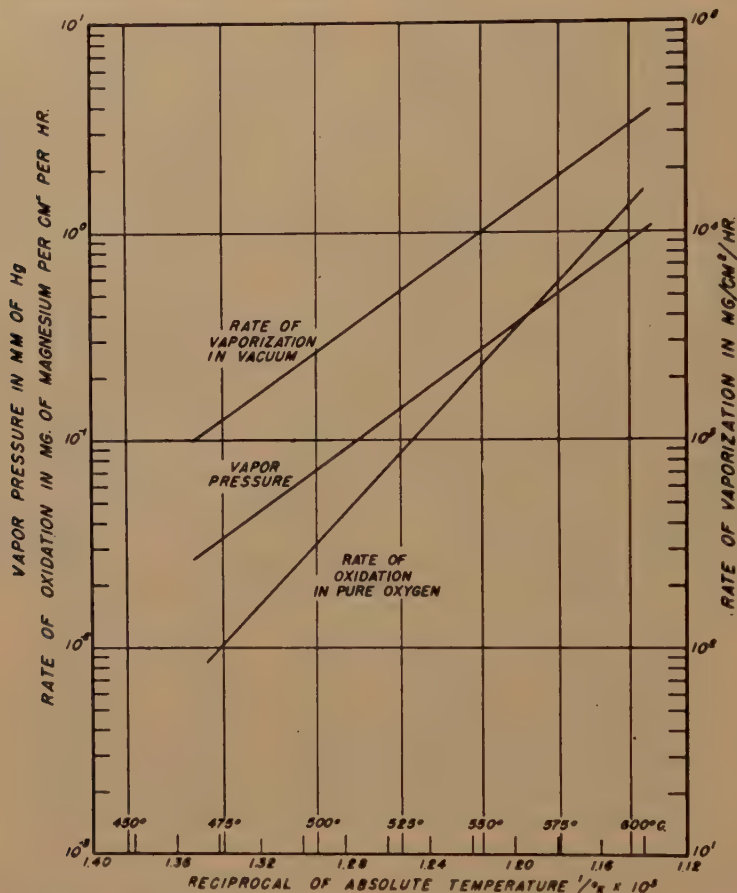


FIG. 23.—COMPARISON OF EFFECTS OF TEMPERATURE UPON RATE OF OXIDATION, RATE OF VAPORIZATION OF MAGNESIUM IN VACUUM AND VAPOR PRESSURE OF PURE MAGNESIUM.

Vapor-pressure data from Coleman and Egerton;¹² rate of vaporization calculated by Langmuir's¹³ equation.

tive to the concentration of the reactants, while first and higher order reactions are distinctly sensitive to the concentration of the reactants. The experiments described have shown no consistent trend in the rate as a function of oxygen pressure (equivalent to oxygen concentration): at reduced oxygen pressure (200 mm.) Gulbransen found a higher rate at 500°C. and a lower rate at 475°C. than was observed

rate of oxidation; in oxygen-nitrogen mixtures, we found smaller rates than in air, both when the oxygen partial pressure was above and when it was below that in air. Thus, it is reasonable to conclude that the reaction is insensitive to pressure and is of the zero order.

Glasstone, Laidler and Eyring¹⁷ give for the rate of the ideal zero-order reaction the expression:

$$v = c_a \frac{kT}{h} e^{-E/RT}$$

where v represents the reaction rate in molecules per square centimeter per second,

rate of the zero-order reaction of oxygen upon magnesium. It is possible, however, to test the validity of the assumptions contained in the equation, as applied to

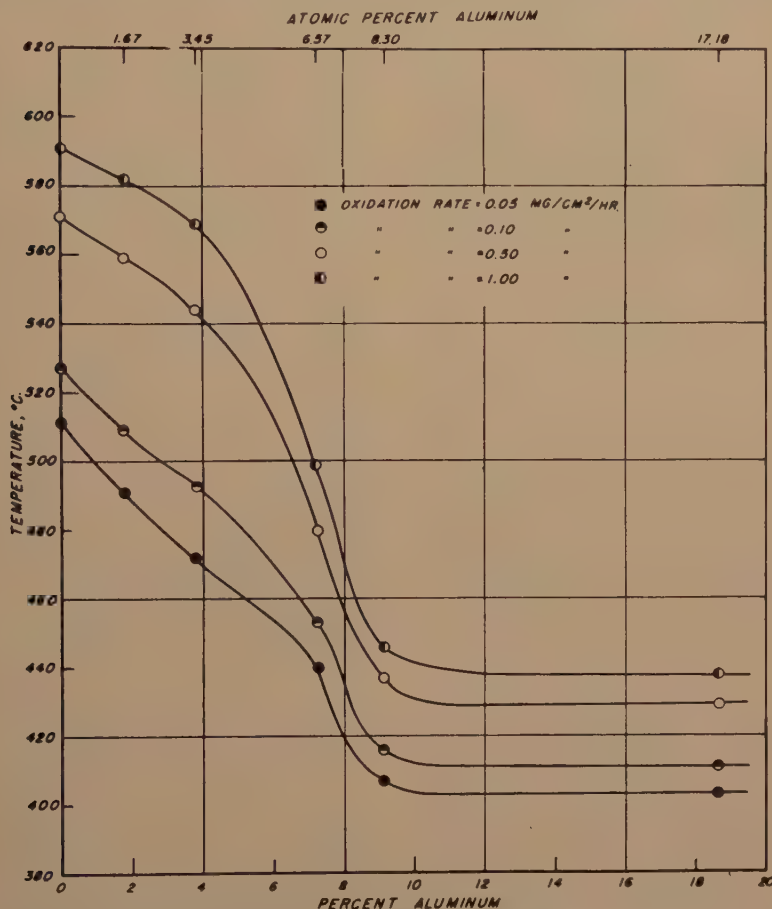


FIG. 24.—EFFECT OF ALUMINUM CONTENT ON TEMPERATURE REQUIRED TO GIVE SPECIFIC RATE OF OXIDATION.

c_a is the number of activated centers per square centimeter of surface (approximately equivalent to the number of atoms in a square centimeter of surface), k is the Boltzmann constant, h Planck's constant, R the gas constant, T the absolute temperature and E the activation energy per mol. In the absence of data from which the activation energy E can be computed, it is not possible to calculate the

the present case, by substituting the measured values of the reaction rate and the activation energy and solving for one of the constants of the equation. If this is done using the rate of 0.032 mg. per sq. cm. per hr. found at 500°C. and the energy of activation 50,500 cal. per mol, it is found that the value of c_a becomes 1.5×10^{15} ; which is to be compared with 1.1×10^{15} atoms in a square centimeter

on the close-packed basal plane of magnesium. For calculations of this kind the agreement is excellent.

It may be concluded, therefore, that the chief criteria of zero-order reaction have been met. The oxidation reaction takes place by the adsorption of a layer of oxygen molecules upon the magnesium surface, with subsequent reaction to form MgO, which does not adhere to the surface. Previous cases of zero-order reaction have involved only catalysis where the products of reaction leave the metal surface as a gas and carry away none of the metal itself.

Although the approximations contained in the computation of c_a cited above really forbid speculation with regard to the difference between the calculated value, 1.5×10^{16} and the number of atoms in a close-packed square centimeter of magnesium, 1.1×10^{16} , the temptation to do so is very strong. For the sake of argument, let it be supposed that there is a real difference in the figures, in the direction indicated; this would mean that there are in effect more activated centers per square centimeter of surface than there are atomic positions in the same area. Such a result might have been anticipated in view of the relatively high vapor pressure of magnesium. If metal vapor is released at the metal surface, some additional oxidation may take place in the vapor phase in front of the metal surface, or the magnesium vapor may become absorbed on an adjacent surface of MgO, where the reaction could proceed with the further adsorption of oxygen. In either case the effective reaction surface would be increased.

Mention has been made of the occurrence of nonprotective oxidation in two consecutive linear stages. The second stage is always faster than the initial stage, and the character of the scale changes from a rather dense, though still porous product, in the initial stage, to a

loose fluffy deposit, composed largely of MgO cubes, in the second stage. These observations can now be related to the mechanism of nonprotective oxidation just proposed. When nonprotective oxidation starts, the metal is already covered with the closely adhering protective film. Upon the rupturing of this protective film any new MgO molecule that forms may be expected to precipitate upon the inner surface of this film, causing it to grow as a dense, polycrystalline body. Such scales have a strong tendency to separate from the metal; upon cooling they always separate and when they reach a thickness of about 0.001 in. they tend to separate at constant temperature. Suppose, now, that the dense scale begins to pull away from the metal, possibly first at isolated points, where the thickness reaches a critical value. There is now substantial space between the metal and the oxide scale. This leaves more room for vapor-phase reaction or its equivalent reaction with magnesium adsorbed on the oxide, and the rate of oxidation increases accordingly. The oxide is no longer being formed exclusively in the immediate neighborhood of the existing scale and the conditions surrounding the condensation of the newly formed MgO may be expected to more nearly approximate those present in combustion; i.e., cubic idiomorphic crystals of MgO may form. Since the MgO cubes are randomly oriented (X-ray and microscopic studies revealed no preferred orientation), their loose packing will maintain the space for continued reaction at the increased rate.

In this connection, it is interesting to recall the observation that the MgO cubes found in loose scales formed at high temperatures were generally smaller than those formed at lower temperatures. This means that the rate of MgO crystal nucleation must be greater at the higher temperatures. This would be true if the effective MgO concentration (or vapor

pressure) were higher at high temperature, which is consistent with the theory proposed.

It remains to consider how the presence of alloying elements can change the rate of nonprotective oxidation. The only alloy that exhibited a decreased rate, as compared with pure magnesium, was the one containing cerium, and in this case only protective oxidation was found except where local breakdown of the film permitted the linear formation of loose oxide. Hence it appears that the only observed effect of alloying upon nonprotective oxidation is an increase in the rate; some elements, of course, had little or no effect. Application of the theoretical equation for the rate of a zero-order reaction to the case of alloys results in both negative and positive deviations in the calculated value of c_a ranging from one to several orders of magnitude, depending upon the value of the experimental energy of activation. Since the controlling factor in this equation at a given temperature is the energy of activation, the consideration of changes in this quantity as a result of alloying is not sufficient to explain the change in the rate of oxidation. Another conceivable reason for an increased rate has occurred to us, but it is not susceptible to quantitative proof with the data at hand: eutectic-forming alloying agents that lower the melting point (virtually all elements involved in the present studies) tend to increase the total vapor pressure over the solid phase; this might be expected to increase the importance of the postulated vapor-phase reaction. Actually, the observed increase in rate resulting from alloying was almost always roughly proportional to the decrease in the melting temperature (solidus) of the alloy. This is best illustrated by considering the temperature at which a given oxidation rate prevails as a function of alloy content. Fig. 24 shows such a series of curves for the magnesium-alumi-

num alloys. The similarity of these curves to the solidus line of the magnesium-aluminum diagram (eutectic temperature = 436°C . and maximum solid solubility = 12.6 per cent Al) indicates at least a qualitative relation between rate of oxidation and melting point.

SUMMARY

The linear oxidation of pure magnesium and of a series of magnesium alloys has been measured within the temperature range 412° to 575°C ., where a loose oxide scale forms. It has been found that the logarithm of the rate is directly proportional to the reciprocal of the absolute temperature. The energy of activation E for the oxidation of magnesium in this range is 50,500 cal. and the action constant A is 6.2×10^{12} mg. per sq. cm. per hr. Alloying increases the rate of oxidation of magnesium whenever the melting temperature is significantly depressed by the alloying element. Magnesium forms a protective oxide film at low temperatures, a nonprotective loose scale at higher temperatures, and may undergo combustion at temperatures approaching the melting point.

A theory of the oxidation of magnesium which has been proposed may be briefly stated as follows: at low temperatures, and in the early stages of oxidation at higher temperatures, normal protective oxidation occurs; when the protective scale reaches a critical thickness it disintegrates spontaneously and a linear zero-order reaction between oxygen gas and magnesium thereafter occurs at or adjacent to the metal surface; at still higher temperatures the rate of evaporation of magnesium becomes so great that the reaction occurs at a considerable distance from the surface and constitutes normal combustion with a flame.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to The Dow Chemical Co. for

the granting of a fellowship to one of them and for the many ways in which assistance was offered in the experimental work and in the preparation of this manuscript. They also wish to acknowledge with thanks the assistance of Miss Helen Louise Uramey, who carried out many of the rate measurements; of Mrs. Kathleen Wells, for the electron microscopy; and of Mrs. Wilma Urquhart, for various phases of the experimental work. Special thanks are also extended to the various members of the faculty of the Carnegie Institute of Technology for the helpful discussions of the manuscript.

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DISCUSSION

(H. Y. Hunsicker presiding)

H. Y. HUNSICKER.*—The authors are to be commended for a very thorough fundamental

* Aluminum Company of America, Cleveland, Ohio.

investigation of a problem that has considerable practical importance.

I would like to ask whether they have measured the extent to which the physical state of the surface affects rate of oxidation.

T. E. LEONTIS (author's reply).—Use of various grades of Aloxite papers produced no significant change in the rate of oxidation. In fact, we went as far as preparing the surface by filing with a very fine file, and that resulted in no change in the rate of oxidation. Surfaces prepared by metallographic polishing were not investigated.

In reply to the part of the question dealing with localized points that might enhance the rate of oxidation, there is a figure in the paper showing that if rolling cracks are present along the edges, the rate of oxidation is much faster along those cracks. In fact, it is almost localized along them.

J. R. BURNS.*—Can you tell what effect a little bit of SO₂ or sulphur might have on the film formed at high temperatures? I mean the role played by SO₂ in heat-treating operations.

T. E. LEONTIS.—We have made experiments that have shown that the additions of sulphur dioxide and carbon dioxide to oxygen at atmospheric pressure will virtually suppress the oxidation at temperatures as high as 550°C. It is known from other studies that the film formed upon the surface of magnesium when SO₂ is present is not magnesium oxide, but magnesium sulphate.

C. E. NELSON.†—Beryllium has a very interesting effect on reducing oxidation rate in both the liquid and solid magnesium. I do not believe there is anything in the paper about that, and I suggest that it would be a valuable field to investigate.

U. R. EVANS.‡—This extensive and accurate survey of the oxidation of pure magnesium is most welcome. The precise rectilinear form of the majority of the curves is particularly satisfactory, since until recently there has been much doubt as to whether or not the

* Wright Field, Dayton, Ohio.

† The Dow Chemical Co., Midland, Michigan.

‡ Cambridge University, England.

oxidation of magnesium followed a straight line.

It may perhaps be useful to say a few words regarding the interpretation. The authors write: "The theory of parabolic oxidation is well developed. Linear oxidation, on the other hand, has received but little attention." The recent development of the theory of parabolic thickening depends largely on the experiments and writings of Wagner,¹⁸ Price,¹⁹ Hoar and Price,²⁰ Price and Thomas,²¹ and Mott²²—papers that deserve very careful study, since they bring out the all-important connection between the velocity constants and the electrical properties of the film substances. As regards linear and logarithmic oxidation, some help may be obtained from the work of Vernon,²³ Finch and Quarrell,²⁴ Tronstad and Höverstad,²⁵ Dunn and Wilkins²⁶ and Vernon, Akeroyd and Stroud.²⁷ It has been suggested that a coherent film, relatively protective and probably pseudomorphic after the metal, is first formed, which breaks up as soon as it exceeds a certain thickness. The relatively porous mass produced by the reversal of the pseudomorphic film to the stable crystal form of oxide is supposed to offer little resistance to the passage of material, and since resistance is due to the pseudomorphic film that maintains a uniform thickness, the rate of growth—in absence of further complications—remains constant. A few years ago, the writer²⁸ put forward a rather similar theory to explain logarithmic thickening, but

more recent results²⁹ suggest that the assumption of a compact film of constant thickness is not necessary to account for the logarithmic growth law.

As regards linear growth also, the two-layer picture as presented in the papers quoted may require some modification in explaining the facts now established by the authors, but if it should be retained to the extent of accepting passage through a compact basal film as the rate-controlling process, then the energy of activation as derived from the temperature coefficient must be accorded a different significance from that apparently assumed by the authors.

However this may be, it is interesting to note that the authors have reached the conclusion that "when the protective film reaches some critical thickness, the exact value of which will depend upon the temperature, the surface contour of the metal, and the composition of the film . . . tensile ruptures appear spontaneously, admitting oxygen gas through the film, and thereby accelerating oxidation."

It would indeed be expected, from elementary principles, that the disruptive transformation from the metastable (pseudomorphic) form of oxide to the stable form will take place spontaneously only when a certain thickness has been reached, as was pointed out by the writer some years ago.³⁰ The formation of stable oxide from the pseudomorphic form (which can often be regarded as the stable form with its parameter unnaturally elongated in one direction and shortened in the other) can, in general, take place only if there is detachment from the metallic basis, at some points at least. If W_A is the work needed per unit area to overcome adhesional forces, and W_C is the energy per unit volume liberated when the distorted form reverts to the undistorted form, the net energy change should be $\gamma W_C - W_A$ per unit area, where γ is the film thickness. Thus the change should, in the case of a flat film, occur spontaneously when γ exceeds W_A/W_C . It may occur at a smaller thickness at points of convex curvature, where the volume per unit area of the surface of separation will exceed γ . This is doubtless one reason why "nonprotective oxidation

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¹⁹ L. E. Price: *Chem. Ind.* (1937) 769.

²⁰ T. P. Hoar and L. E. Price: *Trans. Faraday Soc.* (1938) **34**, 867.

²¹ L. E. Price and G. J. Thomas: *Jnl. Inst. Metals* (1938) **63**, 21, 29.

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²³ W. H. J. Vernon: *Trans. Faraday Soc.* (1927) **23**, 139; *Met. Ind.* (1935) **46**, 239.

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²⁵ L. Tronstad and T. Höverstad: *Trans. Faraday Soc.* (1934) **30**, 1122.

²⁶ J. S. Dunn and F. J. Wilkins: Review of Oxidation and Scaling of Heated Solid Metals, 67. H. M. Stationery Office, 1935.

²⁷ W. H. J. Vernon, E. I. Akeroyd and E. G. Stroud: *Jnl. Inst. Met.* (1939) **65**, 301.

²⁸ U. R. Evans: *Trans. Electrochem. Soc.* (1943) **83**, 335; *Trans. Faraday Soc.* (1945) **41**, 365 (esp. appendix on p. 372).

²⁹ U. R. Evans: Unpublished work.

³⁰ U. R. Evans: *Metallic Corrosion Passivity and Protection*, 69. 1937 Ed. Arnold.

starts preferentially at edges, crannies or imperfections, spreading thence over the entire surface," although clearly other causes could be suggested for the starting of the

the complete disintegration of the protective film at a certain thickness is more reasonable.

Dr. Evans has also shown that the thickness at which the initial film ruptures may be

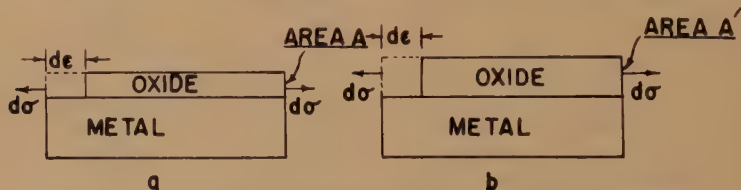


FIG. 25.—RELATION BETWEEN METAL AND OXIDE ON MAGNESIUM.

phenomenon at these points. Actually, however, a certain fraction of the energy could be liberated with only partial detachment, so that a further sudden increase would be expected at a second critical thickness—as is actually observed. Probably this picture, which is sketched with intentional vagueness, will require considerable modification before it becomes fully consistent with the facts, but it is believed that on some such lines will be found an explanation of the experimental data that accords also with observations on other metals.

T. E. LEONTIS and F. N. RHINES (authors' reply).—The remarks of Dr. Evans are indeed welcome. There are a few points upon which the authors would like to comment. Dr. Evans suggests that the rate of linear oxidation is controlled by the passage of reactants through a "compact basal film," which retains a constant thickness during the oxidation process. This assumes that only the outside layers of the film develop fissures, while an inner, compact layer of constant thickness is always maintained. As stated in the discussion of the paper, we believe that at a certain critical thickness, ruptures appear spontaneously throughout the entire film, thus permitting free access of the oxidizing atmosphere to the metal surface. Under these conditions, the rate of oxidation is controlled by the rate of chemical reaction between the metal and oxygen and this we have interpreted in terms of the kinetics of Eyring. With the data at hand, neither hypothesis can be definitely proved, but it appears to us that in the case of magnesium, where the film is under tensile stresses; the picture involving

calculated from a consideration of the energy relationships. This may also be considered in another manner. In Fig. 25 is shown a sketch of the dimensional relations between the metal and the film for the case of magnesium whose oxide occupies less volume than the metal from which it is formed. If $d\epsilon$ is the dimensional difference between the oxide and the metal, then for the oxide film to conform to the metal surface it must extend by $d\epsilon$ introducing a tensile stress $d\sigma$ is given by

$$d\sigma = E d\epsilon$$

where E is the modulus of elasticity of the oxide. This introduces a tensile load P on the area A given by

$$P = A d\sigma$$

which must be counteracted by a shearing force between the metal and the film. As the thickness of the oxide film increases, the tensile load P will increase by virtue of the increased area A_1 and rupture of the film will occur when the shear stresses at the metal-film interface exceed the adherence forces between the metal and the film. This analysis may also be used to explain the separation of the initial, dense oxide scale, which has been observed to form upon magnesium, when a certain critical thickness of 0.001 to 0.002 in. is exceeded.

We would like to reiterate Mr. Nelson's remarks that additions of beryllium to magnesium appear very interesting from the standpoint of oxidation resistance and the subject should be pursued to some extent.

Properties of Cerium-containing Magnesium Alloys at Room and Elevated Temperatures

By T. E. LEONTIS* AND J. P. MURPHY†

(Chicago Meeting, February 1946)

DURING the last few years, the trend in the aircraft and automotive industries has been toward higher and higher operating engine temperatures. This has created considerable interest in the effect of temperature on the properties of alloys. In the magnesium field, it has been recognized for many years that the addition of cerium imparts high strength and good resistance to creep at elevated temperatures. Beck,¹ in his treatise on magnesium, has summarized the work of German investigators. This includes the unpublished data of Menking, showing the increase in strength and hardness of extruded alloys containing 2 to 20 per cent Ce at temperatures from 20° to 300°C. (68° to 572°F.) and the results of Vosskühler, who demonstrated the improved resistance to creep of alloys containing 6 per cent Ce plus 2 per cent Mn and 0.5 per cent Ce plus 2 per cent Mn at 150°C. (302°F.). Wellinger and Keil² have also reported the creep properties of a forged magnesium-cerium-manganese alloy at 200° and 250°C. (392° and 482°F.). Haughton and Prytherch have determined the tensile properties of various forged magnesium alloys containing cerium, cerium plus manganese, cerium plus calcium, cerium plus nickel, cerium plus

nickel plus manganese, and cerium plus cobalt plus manganese at temperatures up to 290°C. (554°F.).

Magnesium-cerium alloys have been used in some commercial applications. It is reported that an alloy containing 3 per cent Ce plus 0.5 per cent Mn plus 0.5 per cent Ca is being used on a forged impeller in Great Britain. Two forged parts made from an alloy with a nominal composition of 5 per cent Ce and 2 per cent Mn have been found on the German BMW-801D aircraft engine. These two forgings consist of a supercharger impeller and a rear cam-follower guide.

In this country, several types of pistons have been made experimentally in both the cast and the forged conditions from an alloy containing 6 per cent Ce plus 2 per cent Mn and in the cast condition from an alloy of magnesium plus 10 per cent Ce. The cast pistons have been tested in various types of internal-combustion engines, with promising results.

This paper presents the results of an extensive investigation on the properties of various cerium-containing magnesium alloys in both the cast and the forged conditions. Data are presented to show the beneficial effects of increasing amounts of cerium on the mechanical properties of magnesium at elevated temperatures. The effects of heat-treatment on the properties of these alloys and the attendant changes in the microstructure are discussed. The alloys investigated most extensively are

Manuscript received at the office of the Institute Nov. 26, 1945. Issued as T.P. 1995 in METALS TECHNOLOGY, April 1946.

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¹ References are at the end of the paper.

listed in Table 1 with their corresponding A.S.T.M. designations. In all tests, the cerium was added as Mischmetal, an alloy

TABLE 1.—*Nominal Composition of Cerium-containing Magnesium Alloys*

Alloy Designation	Nominal Composition, Per Cent	
	Mg+	
	Ce	Mn
E6	6	
E10	10	
EM02	0.5	2
EM22	2	2
EM42	4	2
EM62	6	2
EM102	10	2

containing 45 to 50 per cent Ce, 22 to 25 per cent La, 23 to 27 per cent other rare earths and a rather high impurity content, of which iron is the major part. This material is available from various sources at a price ranging from \$5.00 to \$3.25 per pound, depending on the quantity purchased. Throughout this paper the term "per cent cerium" refers to the total rare-earth content of the alloys.

PREPARATION OF ALLOYS

Melting Practice

The alloys used in this investigation were made in small laboratory melts according to melting and casting techniques previously established as necessary for the production of sound material as discussed in detail by Marande.⁴ Commercial magnesium or Dowmetal M (1.5 to 2.0 per cent Mn) was melted down, depending on whether a magnesium-cerium or a magnesium-cerium-manganese alloy was to be cast. The cerium was added in the form of Mischmetal.

It was necessary to take special precautions in the alloying and casting of these alloys because of two major problems, which are not readily reconcilable: (1) the high reactivity of cerium with the $MgCl_2$ present in the common melting fluxes,⁵

resulting in a high loss of cerium; and (2) the inclusion of flux in the casting resulting from the use of the more fluid flux that does not contain $MgCl_2$. It was found that when the melt was poured immediately after alloying, Dow No. 310 flux containing $MgCl_2$ could be used and still attain a cerium alloying efficiency of 85 to 95 per cent. Alloying was carried out at 1350°F. After the addition of all the Mischmetal and thorough stirring, the temperature was raised to 1400°F. A period of about 15 min. was allowed for the flux to separate from the metal, and finally the surface flux was skimmed off and the melt poured.

Because of the high cost of cerium, it often becomes necessary to remelt scrap. For such operations, and for cases where it was desired to hold a melt for more than one hour, the non- $MgCl_2$ flux, Dow No. 220, was used in order to reduce the loss of cerium to a minimum. To minimize the possibility of flux inclusion in the castings, the following measures were taken. After the meltdown, or at the end of the holding period, the excess flux was skimmed from the surface of the metal, and either Dow No. 310 flux or CaF_2 was added to thicken the remaining fluid flux. A holding period of 15 to 30 min. at the pouring temperature was then allowed before casting in order to settle as much of the flux as possible. The remaining flux was again skimmed from the surface before pouring.

Grain Size Control

Magnesium containing 6 to 10 per cent Ce sand-cast at 1400°F. in the form of standard 0.5-in. test bars has a moderately fine equiaxed grain size of 0.01 to 0.04 in., which is not influenced by subsequent heat-treatment. However, the grain size of these alloys can be markedly changed by either of two factors: (1) manganese content; and (2) pouring temperature.

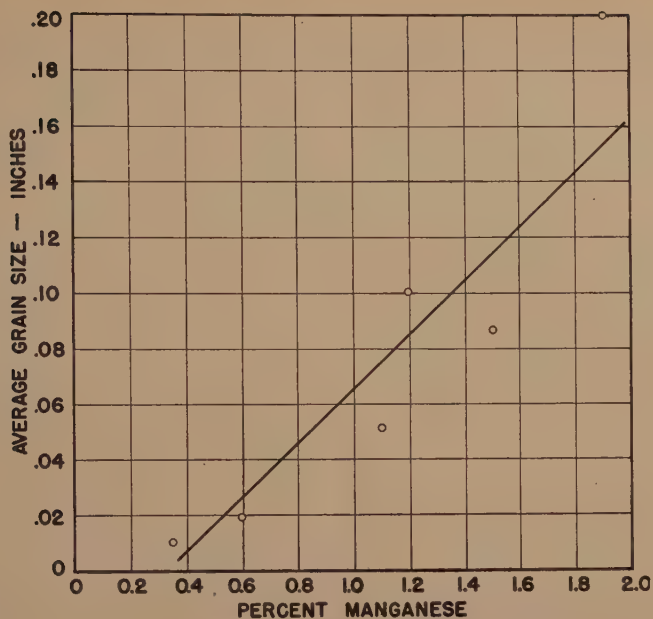


FIG. 1.—EFFECT OF MANGANESE CONTENT ON GRAIN SIZE OF MAGNESIUM ALLOY CONTAINING 6 PER CENT CERIUM POURED AT 1400°F.

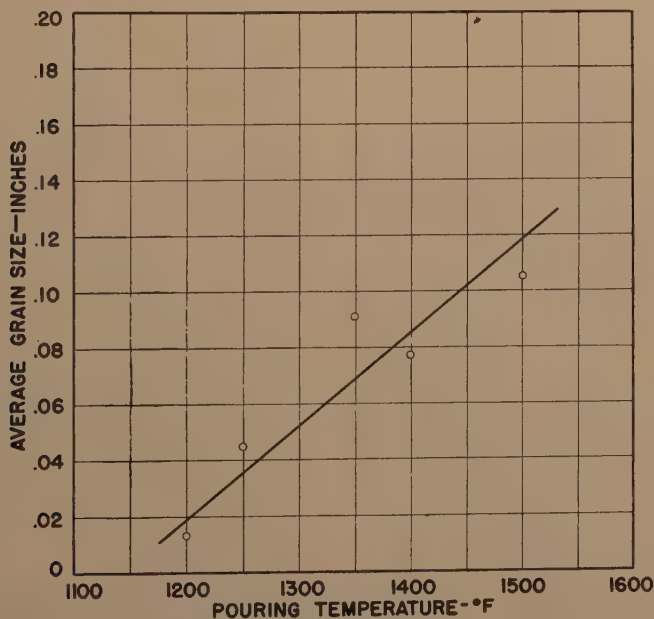


FIG. 2.—EFFECT OF POURING TEMPERATURE ON GRAIN SIZE OF ALLOY EM62.

Additions of manganese to these alloys progressively increase the grain size up to a value of 0.26 in., corresponding to a manganese content of about 2 per cent. Fig. 1 shows the relation between grain size and manganese content in alloys containing 6 per cent Ce. The data on this plot represent the average values of a large number of determinations made at various positions along the length of the standard test bar (6.5 in.). It should be pointed out that variations ranging from 0.02 to 0.20 in. can exist within one test bar; the smallest grain-size values occurring in the reduced section of the test bar.

The results presented in Fig. 1 were based on melts all poured from 1400°F. In Fig. 2 is shown the variation in the grain size of EM62 alloy as a function of pouring temperature. The results plotted are again the average of a large number of determinations, as described above. The effect of increasing pouring temperature on the grain size is apparent. It was also observed that the variation in grain size within a given test bar decreases with decreasing temperature.

A few experiments have been carried out in an attempt to refine the grain size of magnesium-cerium-manganese alloys by the addition of zirconium. The difficulty of maintaining a high manganese content with an appreciable amount of residual zirconium renders these results inconclusive. However, in all tests there was a tendency toward finer grain sizes for equivalent manganese contents whenever zirconium was added to the melt, regardless of the amount that remained in the castings. It was also observed that the zirconium-treated alloys had higher strength properties at room temperatures.

TESTING METHODS

The results on cast alloys presented in this paper were obtained on 0.5-in. standard tension-test bars cast to size. The various heat-treatments applied to the

bars and their attendant influence on the structure and properties are discussed in a later section. The heat-treatments were carried out in circulating air furnaces, which were controlled to $\pm 5^\circ\text{F}$. A concentration of 0.5 per cent SO_2 was maintained in the furnace atmosphere, to prevent excessive oxidation. Because of the high temperatures required for the solution heat-treatment of these alloys, the bars were packed in sand, in order to avoid any sagging.

Tension tests at room and elevated temperatures were carried out on the cast test bars, without machining the as-cast surface, according to A.S.T.M. specifications (E21-43).⁶ One modification was made to the elevated-temperature testing procedure; instead of the specified one hour holding period at temperature before testing, the bars were held at temperature for 10 min. It had been established previously that no difference was caused by the use of this shorter holding period.

Fatigue properties were determined on R. R. Moore rotating-beam machines, using plain and notched specimens with a highly polished surface. The notch used had a radius and depth equal to one tenth the diameter at the base and resulted in a stress-concentration factor of 2. The specimens for fatigue tests were machined from the reduced section of the standard cast test bars.

The creep results are based on tests of 100 hr. duration, carried out on individual vertical creep machines with the load applied through a lever system. The temperature of the furnace and of the specimen, as well as the variation of temperature over the length of the test bar, were controlled to well within the limits of A.S.T.M. specifications (E22-41). The extensions were measured with an optical extensometer having a unit sensitivity of 10^{-6} and the unit accuracy of the readings is believed to be at least $\pm 2 \times 10^{-5}$. A set of typical creep curves for alloy EM102

at 300°F. is shown in Fig. 3 for three different stress levels. It is apparent from the curves that during the 100-hr. test, the secondary stage of creep is not attained

between the stress and creep extension on this method of plotting facilitates the interpolation or extrapolation for obtaining the creep limit. In both Figs. 3 and 4,

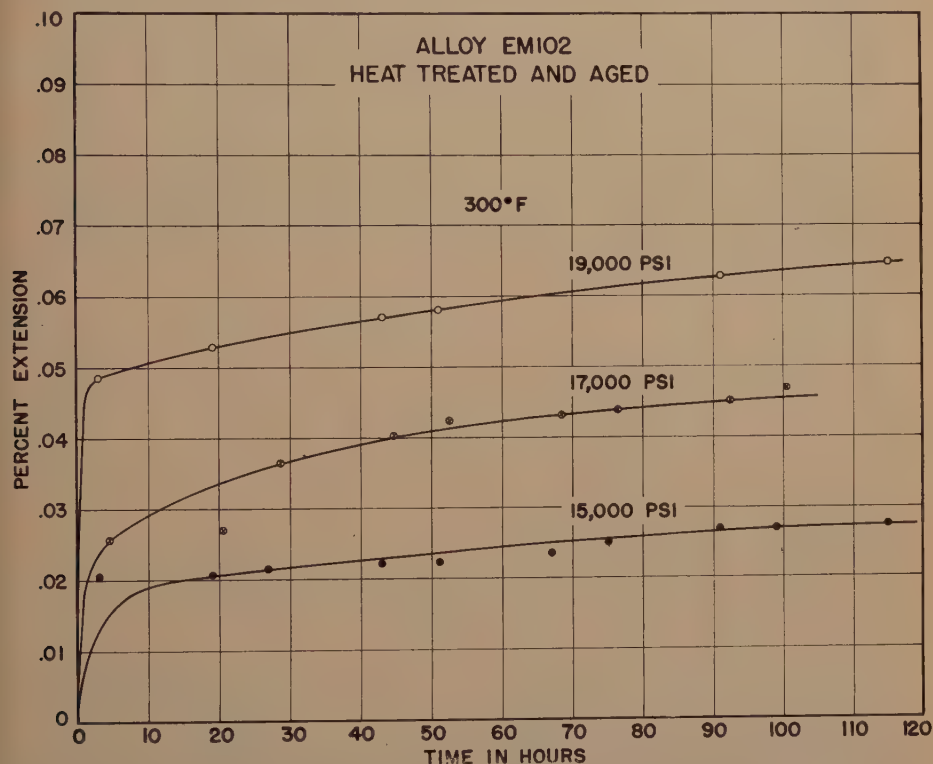


Fig. 3.—TYPICAL CURVES OF EXTENSION IN CREEP VERSUS TIME FOR ALLOY EM102 AT 300°F.

and the material continues to deform at a decreasing rate. For this reason, no significance has been attached to the creep rates obtained in these tests, therefore the conventional methods of analyzing creep data cannot be applied.

As a basis for comparison, the *creep limit*, defined as the stress required to produce an extension of 0.1 per cent in 100 hr. in creep is used throughout this paper. This is obtained by plotting on a log-log scale the extension obtained in 100 hr. against the corresponding stress. Fig. 4 shows a series of such curves for the case of EM102 alloy at four temperatures. The linearity in the relation

only the extensions obtained as a result of creep are plotted; the initial deformation during loading is neglected. It is felt that this interpretation of the creep data yields a basis of comparison that is at least qualitatively, if not quantitatively, related to the results to be obtained from a consideration of creep rates during the secondary stage of the process.

The Brinell hardness was determined in all tests from impressions made with a 10-mm. steel ball using a 500 kg. load applied for 30 sec. In order to obtain the hardness at elevated temperatures, a constant-temperature oil bath, which was controlled to $\pm 1^\circ\text{F}$., was used. The speci-

mens were preheated in the oil for at least 10 min. before the load was applied, and the steel ball as well as part of the holder was kept submerged in the oil during testing.

solution of the specimen took place before the end of that time.

Any other special tests that were carried out will be discussed in conjunction with the discussion of the results.

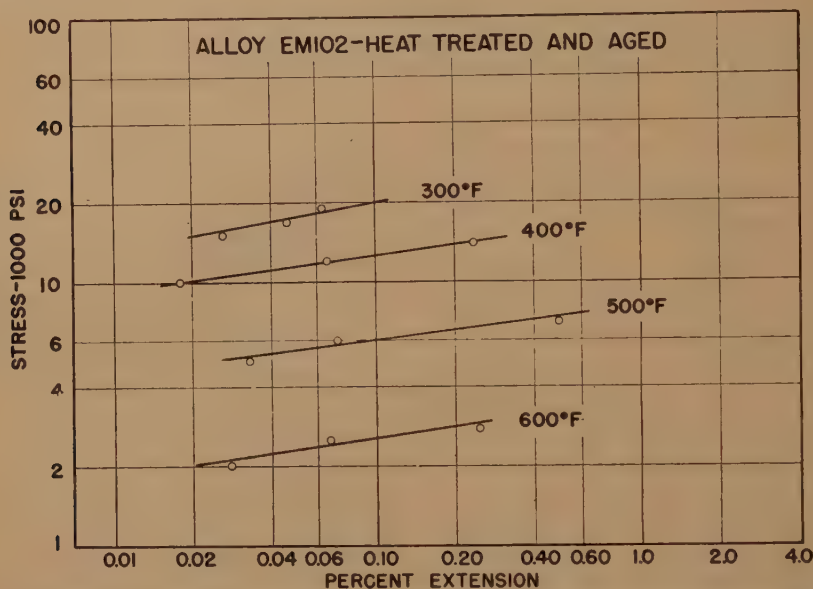


FIG. 4.—TYPICAL CURVES OF EXTENSION IN CREEP VERSUS CREEP STRESS FOR ALLOY EM102.

The electrical conductivity was determined from resistance measurements made with a Kelvin bridge in a constant-temperature room held at 95°F. The conductivity values were corrected to 68°F. (20°C.) using the temperature coefficient for pure magnesium (0.004). Because of the limited solid solubility of cerium in magnesium, it is believed that the coefficient for cerium-containing alloys will not be much lower; certainly the reported conductivity values are accurate to 1 or 2 per cent. The thermal conductivities were obtained from the measured electrical conductivities by means of an empirically established correction to the Wiedemann-Franz ratio.

The corrosion rates are based on alternate immersion tests in 3 per cent NaCl solution at 95°F.; the tests were carried out for a period of 14 days unless complete

HEAT-TREATMENT OF CAST ALLOYS

Metallography

The two principal components of Misch-metal, cerium and lanthanum, form analogous constitutional systems with magnesium.¹ Investigators of these systems have been beset with the difficulty of obtaining the individual rare earth elements in pure form. For this reason, the various temperatures reported must be taken with reservation, since the determinations may not necessarily have been made with pure binary alloys.

In magnesium-rich alloys, the rare earth elements are present as the intermetallic compounds Mg_2Ce and Mg_2La , both of which form by a peritectic reaction between the molten phase and the compounds Mg_3Ce and Mg_3La , respectively. The maximum solid solubility

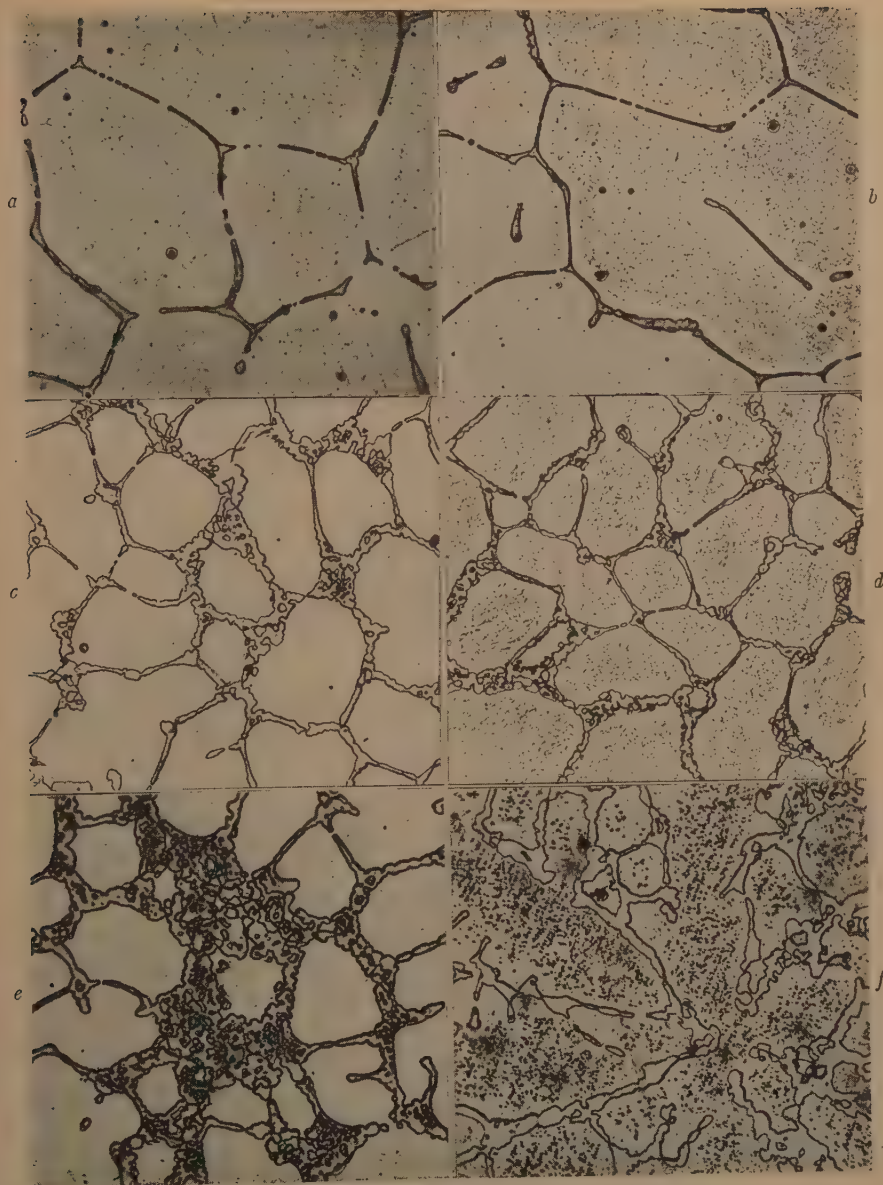


FIG. 5.—MICROSTRUCTURE OF SAND-CAST MAGNESIUM-CERIUM ALLOYS. $\times 250$.

a. 1.29 per cent Ce as-cast. *b.* 1.29 per cent Ce stabilized at 600°F. (16 hr.). *c.* 6.06 per cent Ce as-cast. *d.* 6.06 per cent Ce stabilized at 600°F. (16 hr.). *e.* 10.11 per cent Ce as-cast. *f.* 10.11 per cent Ce stabilized at 600°F. (16 hr.).



FIG. 6.—EFFECT OF HEAT-TREATMENT ON MICROSTRUCTURE OF SAND-CAST MAGNESIUM-CERIUM ALLOYS. $\times 250$.

a. 1.29 per cent Ce heat-treated. *b.* 1.29 per cent Ce heat-treated and aged. *c.* 1.29 per cent Ce heat-treated and stabilized. *d.* 6.06 per cent Ce heat-treated. *e.* 6.06 per cent Ce heat-treated and aged. *f.* 6.06 per cent Ce heat-treated and stabilized.

of cerium in magnesium is reported by Haughton and Schofield⁷ as 1.6 per cent, while Weibke and Schmidt⁸ find it to be 2.2 per cent. According to the latter authors, lanthanum dissolves to an extent of 2.0 per cent at the eutectic temperature. The solid solubility in both cases decreases rapidly from these values with decreasing temperature to a negligible value at room temperature. In view of the marked similarity between the magnesium-cerium and the magnesium-lanthanum systems, it is felt that the structures and heat-treating characteristics of the alloys made with Mischmetal can be safely discussed in terms of the phase diagram of the magnesium-cerium system.

The eutectic temperature of alloys made by the addition of Mischmetal, with and without manganese present, has been determined metallographically to lie between 1080° and 1090°F. On the basis of these data, the heat-treating temperature for obtaining the maximum amount of solution without causing liquation was set at 1070°F. Conductivity measurements on alloys containing 6 and 10 per cent cerium have shown that the maximum amount of solution of compound is attained in $\frac{1}{2}$ hr. at this temperature. However, a 24-hr. period for solution heat-treatment was used for all the work reported herein, in order to obtain complete coalescence of the undissolvable compound. The metallography of magnesium-cerium and magnesium-cerium-manganese alloys has been carefully investigated during the course of this work. In the following paragraphs a summary of the observations on the microstructure and the influence of various heat-treatments thereon is given. The structures presented in the accompanying micrographs were all revealed by etching with the standard acetic glycol etchant (20 parts glacial acetic acid plus 1 part concentrated nitric acid plus 60 parts ethylene glycol plus 19 parts distilled water).

The as-cast structures of alloys containing 1, 6, and 10 per cent Ce are shown in Figs. 5*a*, *c*, and *e*, respectively. The structure of 1 per cent Ce alloy consists prin-

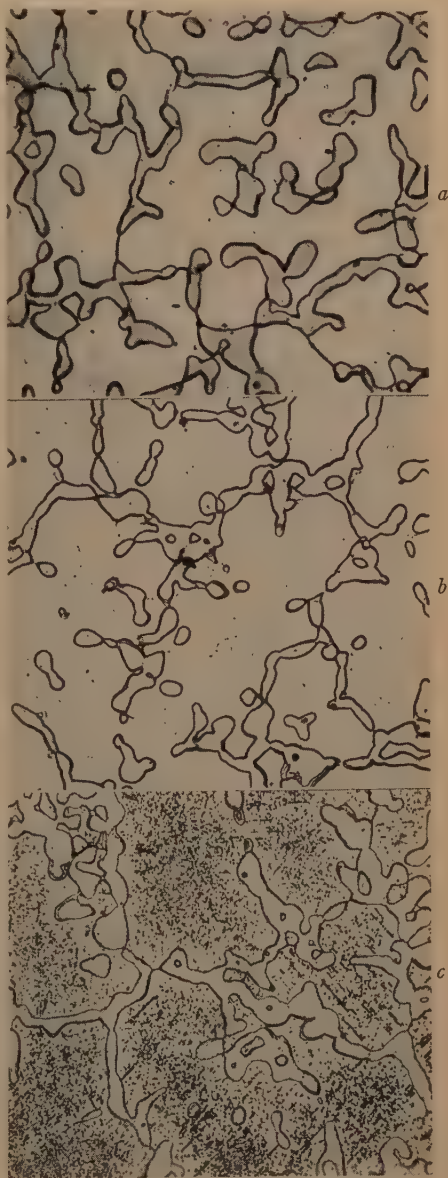


FIG. 7.—EFFECT OF HEAT-TREATMENT ON MICROSTRUCTURE OF SAND-CAST MAGNESIUM + 10.11 PER CENT CERIUM ALLOY. $\times 250$.

a. Heat-treated. *b*. Heat-treated and aged. *c*. Heat-treated and stabilized.

cipally of the primary alpha phase, magnesium solid solution, with a small amount of eutectic (alpha phase plus Mg_2Ce). Actually, in this alloy the eutectic is

in this alloy indicates that coring has taken place, since its composition is well below the reported maximum solid solubility limit. The structures of the 6 and



FIG. 8.—ELECTRON MICROGRAPHS OF CERIUM-CONTAINING MAGNESIUM ALLOYS. METHYL IODIDE ETCHANT.¹¹ $\times 5000$.

a. 6.06 per cent Ce heat-treated. *b.* 6.06 per cent Ce heat-treated and aged. *c.* 6.10 per cent Ce + 1.9 per cent Mn heat-treated. *d.* 6.10 per cent Ce + 1.9 per cent Mn heat-treated and aged.

completely divorced, so that the interdendritic constituent is the intermetallic compound Mg_2Ce . The presence of eutectic

10 per cent Ce alloys show that the alpha phase is completely enveloped by a continuous network of the eutectic within

which the continuous phase is the intermetallic compound (Figs. 5c and e). When these alloys are stabilized from the as-cast condition at 600°F. for 16 hr. (SCS condition), a coarse precipitate appears throughout the alpha phase (Figs. 5b, d, and f), indicating that a considerable amount of cerium is retained in solid solution during cooling from the solidification temperature. No other structural changes result from this heat-treatment.

The effect of heat-treating at 1070°F. (HT condition) on the structure of these alloys is illustrated by Figs. 6a, 6d, and 7a. A small amount of undissolved compound still persists in the alloy containing 1 per cent Ce. This indicates that either the solid solubility of cerium or lanthanum in magnesium is considerably lower than the reported value or that the solubility of the other rare earth elements present in Mischmetal is negligible. The important change in the 6 and 10 per cent Ce alloys is the breakup of the continuity of the eutectic network and the coalescence of the compound into rounded or spheroidal particles. Figs. 6b, 6e, and 7b show the microstructure after aging from the heat-treated condition at 400°F. for 16 hr. (HTA condition). This aging treatment does not result in any visible precipitation under the light microscope in the 6 and 10 per cent Ce alloys. The structure of the alloys after the heat-treated material has been stabilized at 600°F. for 16 hr. (HTS condition) reveals the presence of a very heavy, coarse precipitate throughout the alpha phase (Figs. 6c, 6f, and 7c).

The presence of precipitate in the alloys after aging at 400°F. for 16 hr. has been detected by means of the electron microscope. Fig. 8 shows the electron micrographs of both alloy E6 and an alloy containing manganese, EM62, in both the HT and HTA conditions. Although a small amount of precipitate is visible in alloy E6 in the HT condition, resulting from the relatively slow air cool, the amount increases perceptibly upon aging.

The manganese-containing magnesium-cerium alloys have been investigated more completely. Examination of a series of alloys containing 1.4 to 1.7 per cent Mn

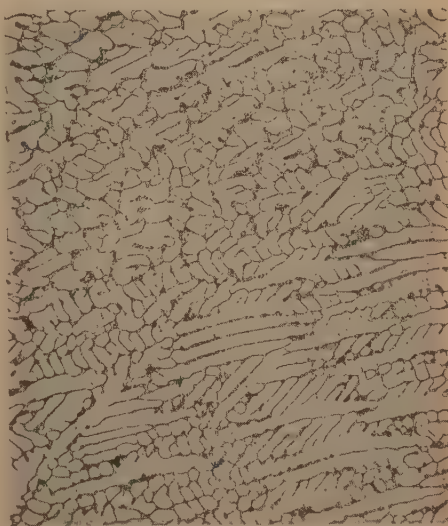


FIG. 9.—DENDRITIC STRUCTURE OF ALLOY EM62. $\times 50$.

with the cerium content varying from 0.5 to 17 per cent has revealed two important structural features: (1) continuity in the eutectic network is attained at approximately 4 per cent Ce; with increasing cerium content, the relative amount of eutectic to alpha phase increases; and (2) the presence of manganese results in a large columnar grain size with a markedly coarser dendritic pattern within each grain. This latter feature is clearly illustrated by the micrograph at a low magnification shown in Fig. 9.

The microstructures of alloys EM62 and EM102 in the as-cast and various heat-treated conditions are illustrated in Figs. 10 and 11. The markedly coarser dendritic structure is apparent in the structures of the as-cast and SCS conditions as compared with the structure of E6 and E10 alloys. The structures of the heat-treated conditions again show the breakup of the eutectic network and the corresponding changes upon aging and stabiliz-

ing. Comparison with the manganese-free alloys shows that slightly less compound remains undissolved in the alloys containing manganese. This effect is further

mined for various alloys and are summarized in Table 2. The increase in conductivity upon stabilizing from the as-cast condition is another indication of the

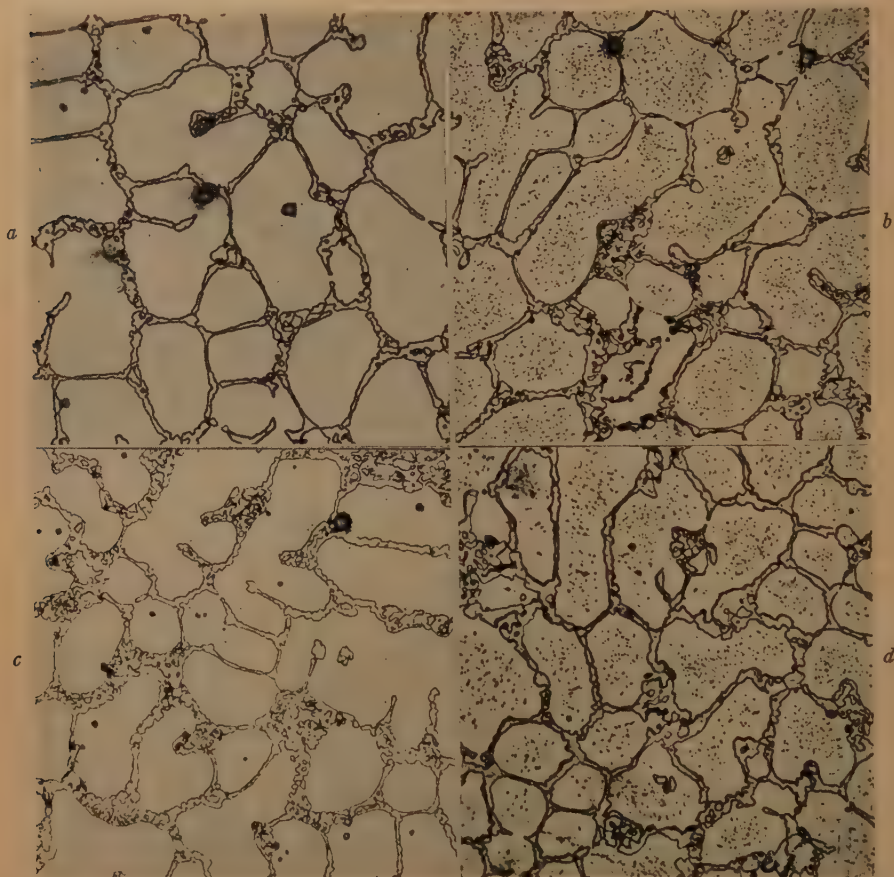


FIG. 10.—MICROSTRUCTURE OF SAND-CAST MAGNESIUM-CERIUM-MANGANESE ALLOYS. $\times 250$.
a. 6.10 per cent Ce + 1.9 per cent Mn as-cast. *b.* 6.10 per cent Ce + 1.9 per cent Mn stabilized at 600°F. (16 hr.). *c.* 9.78 per cent Ce + 1.54 per cent Mn as-cast. *d.* 9.78 per cent Ce + 1.54 per cent Mn stabilized at 600°F. (16 hr.).

illustrated by the changes in conductivity and dimensions resulting from heat-treatment and aging as described in the following paragraphs.

Conductivity

The changes in electrical conductivity resulting from heat-treatment and aging at various temperatures have been deter-

retention of cerium in solid solution with magnesium upon solidification. The conductivity values obtained after heat-treating at 1070°F., followed by quenching in cold water in order to retain the maximum amount of cerium in solution, show that the addition of manganese to each alloy yields a lower value. This is believed to be due to an increase in the solid solu-

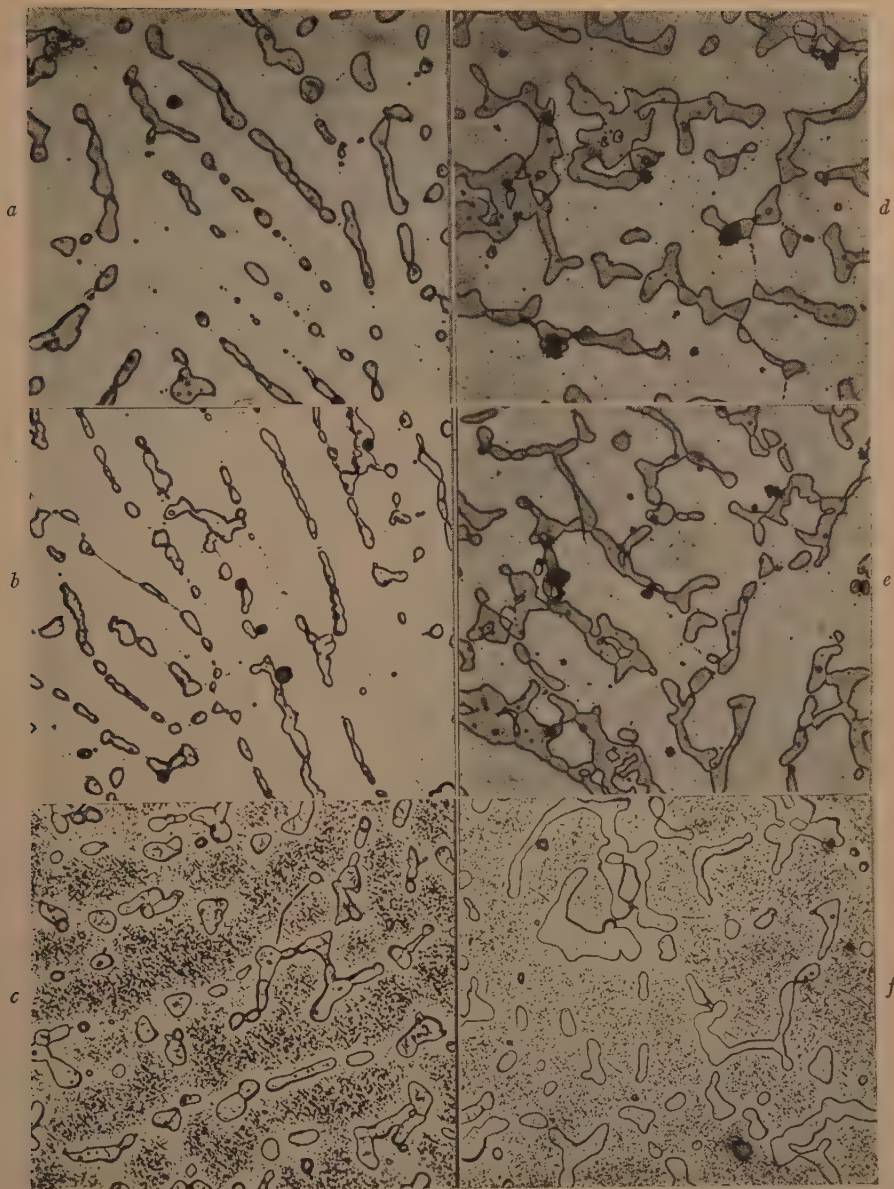


FIG. 11.—EFFECT OF HEAT-TREATMENT ON MICROSTRUCTURE OF SAND-CAST MAGNESIUM-CERIUM-MANGANESE ALLOYS.

a. 6.10 per cent Ce + 1.9 per cent Mn heat-treated. *b.* 6.10 per cent Ce + 1.9 per cent Mn heat-treated and aged. *c.* 6.10 per cent Ce + 1.9 per cent Mn heat-treated and stabilized. *d.* 9.78 per cent Ce + 1.54 per cent Mn heat-treated. *e.* 9.78 per cent Ce + 1.54 per cent Mn heat-treated and aged. *f.* 9.78 per cent Ce + 1.54 per cent Mn heat-treated and stabilized.

bility of cerium in magnesium as a result of the presence of manganese. This belief is strengthened by the observation that heat-treating a cast alloy of magnesium

plain cerium alloys is a further indication of the increase in solid solubility at the heat-treating temperature as a result of the presence of manganese.

TABLE 2.—*Effect of Heat-treatment and Aging on Electrical Conductivity of Sand-cast Cerium-containing Magnesium Alloys*
Electrical Conductivity, Microhm⁻¹-centimeters⁻¹ at 20°C. (68°F.)

Alloy		As Cast	SCS	HTQ	HTQ + Aged 16 Hr. at Indicated Temperatures							
Mg+					400°F.	In- crease	500°F.	In- crease	600°F.	In- crease	700°F.	In- crease
Ce, %	Mn, %											
1.29		0.203		0.178	0.198	0.020	0.215	0.037	0.215	0.037	0.214	0.036
6.06		0.156	0.172	0.127	0.157	0.030	0.167	0.040	0.171	0.044	0.167	0.040
8.1		0.146	0.164	0.119	0.138	0.019	0.156	0.037	0.159	0.040	0.157	0.038
6.19	1.9	0.116	0.155	0.104	0.123	0.019	0.144	0.040	0.166	0.062	0.160	0.056
7.3	1.79	0.112	0.153	0.101	0.119	0.018	0.137	0.036	0.162	0.061	0.158	0.057

containing 2 per cent manganese at the same temperature causes erratic increase in the conductivity rather than a decrease, and by the results of measurements of the dimensional changes accompanying the aging of these alloys to be described in the following section. These deductions are confirmed by the effects of aging on the conductivity. In all tests the conductivity after 16 hr. aging increases with increasing aging temperature up to 600°F. At 700°F. there is a slight drop in the value, probably caused by a perceptible increase in solid solubility at that temperature. The rate of aging as measured by the change in conductivity with aging time is much slower for the manganese-containing alloys than for the corresponding manganese-free alloys; whereas the magnesium-cerium alloys are believed to be very close to their equilibrium values after aging 16 hr. at 500°, 600°, and 700°F., the magnesium-cerium-manganese alloys are still far from equilibrium after 16 hr. at 400° and 500°F., and even at 600° and 700°F. the conductivity of the 8 per cent Ce + 2 per cent Mn alloy is still rising. The much greater increase in the conductivity of the manganese-containing alloys upon aging at 600° and 700°F. than the corresponding

Dimensional Changes Accompanying Aging

The dimensional changes occurring during the aging of cerium-containing magnesium alloys were followed as a function of aging time at 400°, 500°, 600°, and 700°F. subsequent to heat-treatment. These determinations were made on sand-cast test bar, the ends of which were faced to a constant length of 5.7 ± 0.05 in. All measurements of length were made at periodic intervals of aging with a dial gauge mounted on a specially constructed fixture. The smallest division on the gauge was 0.0001 in. and readings could be reproduced to 0.00005 in. The measurements were made in a constant-temperature room after at least one hour had been allowed for the bars to attain an equilibrium temperature. The figures for permanent change in length are believed to be accurate to ± 0.001 per cent.

Fig. 12 shows a set of typical curves for the case of alloy E10, starting with the heat-treated condition. The important observation in these experiments is that precipitation from a solid solution of magnesium-containing cerium results in a dimensional contraction. This is in line with the data of Weibke and Schmidt,⁸

whose X-ray measurements show that lanthanum expands the magnesium lattice. Cerium would be expected to have the same effect on the dimensions of the magnesium

periods as short as 2 hr. at temperatures between 400° and 700°F., so that a contraction of 0.01 per cent or less will result upon subsequent exposure to temperatures

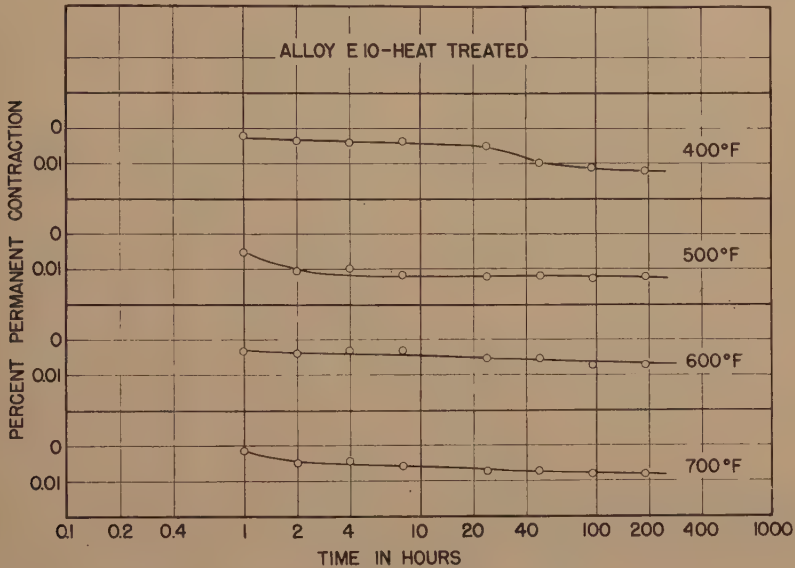


FIG. 12.—TYPICAL CURVES OF PERMANENT CONTRACTION VERSUS AGING TIME AND TEMPERATURE FOR ALLOY E10.

lattice, since its atomic radius, as that of lanthanum, is greater than the atomic radius of magnesium. The complete results of measurements on various alloys are summarized in Table 3. Measurements were made on four different alloys, in each case starting with three heat-treated conditions, HT, HTA, and HTS. The data show that the alloys containing manganese exhibit considerably larger changes upon aging than the manganese-free alloys. Since it is known that manganese contracts the magnesium lattice,¹ it can be now definitely stated that it is the solubility of the cerium in magnesium that is increased by the presence of manganese, rather than that of manganese as a result of the addition of cerium.

The results of these experiments show that magnesium-cerium alloys can be dimensionally stabilized by aging for

TABLE 3.—*Dimensional Changes Accompanying Aging of Sand-cast Cerium-containing Magnesium Alloys*

Alloy	Initial Condition	Permanent Contraction in 192 Hr. at Indicated Temperature, Per Cent			
		400°F.	500°F.	600°F.	700°F.
E6.....	HT	0.014	0.010	0.007	0.006
	HTA	0.008	0.004	0.006	0.003
	HTS	0.009	0.007	0.002	0.004
E10.....	HT	0.012	0.012	0.006	0.008
	HTA	0.007	0.004	0.007	0.004
	HTS	0.008	0.006	0.006	0.004
EM62.....	HT	0.011	0.022	0.022	0.016
	HTA	0.007	0.017	0.015	0.017
	HTS	0.004	0.010	0.010	0.008
Mg + 7.3 per cent Ce + 1.79 per cent Mn.....	HT	0.017	0.018	0.018	0.021
	HTA	0.011	0.017	0.012	0.010
	HTS	0.004	0.005	0.006	0.006

up to 700°F. Magnesium-cerium-manganese alloys, however, require an aging treatment of 16 hr. at 600°F. in order to

attain the same degree of dimensional stability.

PROPERTIES OF CAST ALLOYS

Magnesium-cerium Alloys

The effect of increasing amounts of cerium on the tensile properties of magnesium is shown in Fig. 13. The results for both the as-cast and the heat-treated and aged (HTA) conditions show a linear increase in yield strength with cerium content up to 6 per cent. The elongation decreases rapidly with increasing amounts of cerium. Both the tensile and the tensile yield strengths are increased by heat-treatment.

The effect of solution heat-treatment alone and followed by aging on the mechanical properties of alloys containing 6 and 10 per cent Ce is illustrated by the

TABLE 4.—*Effect of Heat-treating and Aging on Mechanical Properties of Sand-cast Cerium-containing Magnesium Alloys*

Alloy	Heat Treatment	Elongation in 2 In., Per Cent	Tensile Yield Strength*	Tensile Strength*	Brinell Hardness No.
E6	As cast	1.0	14.7	15.9	54.5
	SCS	1.0	13.5	15.9	53.4
	HT	2.0	12.5	16.4	48.9
	HTA	0.5	16.0	21.7	58.7
	HTS	0.5	13.6	18.2	52.3
E10	As cast	0		17.0	64.5
	SCS	0		16.4	63.6
	HT	1.0	15.9	17.1	61.2
	HTA	0.5	19.1	20.7	68.0
	HTS	1.0	17.0	17.8	63.8
EM62	As cast	0	13.1	14.3	53.3
	SCS	0	13.3	13.8	55.6
	HT	1.0	10.0	12.6	50.5
	HTA	0.5	14.3	16.8	56.6
	HTS	1.0	12.5	15.9	53.0
EM102	As cast	0.5	16.9	18.2	63.4
	SCS	0	17.6	17.9	60.6
	HT	1.0	13.6	17.0	57.5
	HTA	0.5	18.5	19.8	65.9
	HTS	0.5	13.4	16.8	61.5

* 1000 lb. per sq. inch.

data in Table 4, together with the corresponding data for the same alloys containing manganese. The yield strength and hardness decrease somewhat from the corresponding values in the as-cast condition upon solution heat-treatment, while

the tensile strength is not affected. Aging at 400°F. for 16 hr. causes about the same increase in both the yield strength and the tensile strength, and the resulting properties are definitely superior to the as-cast properties. Stabilizing at 600°F. for 16 hr. after solution heat-treatment decreases both the strength properties and the hardness slightly.

The static properties of alloys containing 6 and 10 per cent Ce are plotted as a function of temperature in Figs. 14 and 15, respectively, for both the SCS and the HTA conditions. The important feature in these results is the retention of high strength and hardness at elevated temperature. Increasing the cerium content from 6 to 10 per cent increases the yield strength and hardness in both the SCS and HTA conditions over the entire temperature range, while the benefits of the higher cerium content on the tensile strength are apparent only at temperatures above 400°F. The absence of an increase in the tensile strength corresponding to the increase in the yield strength and hardness in the 10 per cent Ce alloy is undoubtedly due to the presence of a considerably larger amount of undissolved intermetallic compound, which renders the alloy brittle at low temperatures. This is further illustrated by the negligible value of the elongation at temperatures below 400°F. and the markedly lower values at higher temperatures compared with those of the 6 per cent alloy.

It was mentioned earlier that one of the most important properties of magnesium-cerium alloys is their relatively high resistance to creep. The values of the creep limit determined by the method outlined earlier will be found in Table 5. The 100-hr. creep test is admittedly too short for obtaining data of great engineering significance. Furthermore, the method of analyzing the data is somewhat arbitrary. The value of the creep limit so obtained for most of the cerium-containing alloys

at 300°F. is well above the yield strength, and in some cases it is equal to the tensile strength. This is a result of the brevity of the 100-hr. test. Because of this short

Comparison of alloy E6 with E10 can be made only at 300°F. Increasing the cerium content results in a significant increase in the resistance to creep, espe-

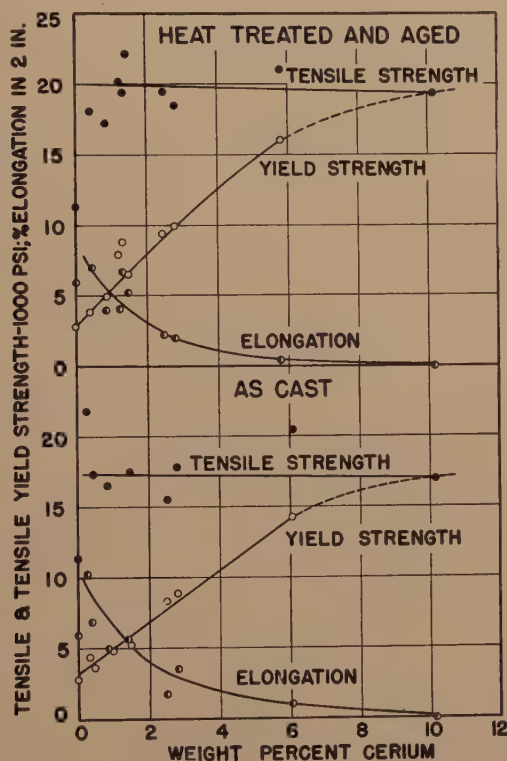


FIG. 13.—EFFECT OF CERMIUM CONTENT ON TENSILE PROPERTIES OF MAGNESIUM.

duration of testing, it was necessary to load the specimens at such stress that a measurable amount of creep would take place during the period of the test. Furthermore, in the determination of the creep limit, no account was taken of the extension occurring during the application of the load. However, although it is fully appreciated that great engineering significance cannot be attached to the creep properties as reported herein, still the results are considered to be of value for comparative purposes. Tests of 1000 hr. duration are now in progress and the results thereof will be reported at a later date.

cially in the HTA condition. The beneficial effect of heat-treatment is seen by the increase in the creep limit at 300°F. from 10,500 to 14,500 lb. per sq. in. for alloy E6 and from 12,700 to 18,500 lb. per sq. in. for alloy E10. The increase due to heat-treatment in the creep limit of alloy E10 at 400°F. is considerably less than at 300°F., and at temperatures above 400°F. the differences become insignificant.

Fatigue properties determined on R. R. Moore rotating-beam machines are also tabulated in Table 5. Again, there is an improvement in going from 6 to 10 per

TABLE 5.—Comparison of Properties of Sand-cast Cerium-containing Magnesium Alloys with Dowmetal H at Room and Elevated Temperatures

Temperature, Deg. F.	Alloy	Heat Treat- ment	Tensile Properties			Brinell Hardness No.	Creep Limits ^b	Fatigue Properties ^{c,d} 1000 Lb. per Sq. In. to Indicated Life					
			Elongation, Per Cent	Yield Str. ^b	Tensile Str. ^b			10 ⁵ Cycles			10 ⁶ Cycles		
								S _p	S _a	N.F.	S _p	S _a	N.F.
Room	E6	SCS	1.0	14.2	17.7	50.7		9.5	8.0	0.84	5.0	4.0	0.80
	E6	HTA	0.5	16.2	21.0	58.2		13.5	11.0	0.81	9.0	6.0	0.67
	EM62	SCS	0.5	13.7	17.9	56.0		10.0	7.0	0.70	7.0	3.5	0.50
	EM62	HTA	0.0	16.3	19.3	60.5		11.5	11.5	1.00	7.0	5.0	0.71
	E10	SCS	0.0		16.2	63.6		12.0	9.0	0.75	11.0	5.0	0.71
	E10	HTA	0.5		19.1	69.0		13.5	10.0	0.74	10.5	8.0	0.76
	EM102	SCS	0.0		17.2	60.6							
	EM102	HTA	0.5	18.5	19.8	65.9							
	DMH ^a	HTS ^a	7.0	17.8	38.7	60.5	20.7	21.0	14.0	0.67	15.0	9.5	0.63
	E6	SCS	2.5	10.2	17.5	41.3	10.5	8.5	7.0	0.82	4.0	2.5	0.62
300 ^d	E6	HTA	3.0	15.9	20.5	48.3	14.2	13.5	8.0	0.59	8.0	4.5	0.56
	EM62	SCS	1.2	11.9	15.8	48.0	11.8	8.5	8.0	0.94	4.0	4.5	1.10
	EM62	HTA	2.0	13.9	16.3	46.8	17.0	11.5	9.5	0.83	8.5	5.5	0.65
	E10	SCS	0.0	14.6	16.6	51.8	12.7	10.0	7.0	0.82	6.5	3.5	0.54
	E10	HTA	1.0	16.3	19.8	58.3	18.5	13.0	10.0	0.77	9.0	6.5	0.72
	EM102	SCS	1.0	12.3	16.8	53.2	12.8						
	EM102	HTA	0.5	16.0	19.9	55.2	20.0						
	DMH	HTS	40.3	14.2	27.0	51.0	4.3	13.5	10.0	0.74	9.5	5.0	0.53
	E6	SCS	6.0	9.1	18.5	36.9							
	E6	HTA	3.5	14.7	18.7	46.4							
400	EM62	SCS	1.2	11.0	15.9	43.0	8.4						
	EM62	HTA	2.0	13.9	17.7	44.4							
	E10	SCS	1.0	12.5	17.0	48.3		9.2					
	E10	HTA	1.8	16.1	19.6	54.7	10.4						
	EM102	SCS	2.1	12.0	17.4	47.5							
	EM102	HTA	0.5	15.2	19.7	52.3	12.5						
	DMH	HTS		12.0	17.5	37.2							
	E6	SCS	6.2	8.3	18.8	35.2							
	E6	HTA	10.7	8.7	16.1	40.2							
	EM62	SCS	2.1	9.8	15.3	36.5	4.2						
500	EM62	HTA	4.5	11.3	17.1	36.6							
	E10	SCS	1.3	10.8	16.8	43.0	4.0						
	E10	HTA	2.0	14.4	18.4	42.0	4.4						
	EM102	SCS	2.6	10.8	18.0	45.7							
	EM102	HTA	1.5	12.7	19.8	43.0	6.0						
	DMH	HTS		9.0	12.0	25.4							
	E6	SCS	40.0	5.9	13.1	26.1							
	E6	HTA	41.7	6.7	11.4	24.8							
	EM62	SCS	19.0	8.1	13.8	23.5	2.4						
	EM62	HTA	21.5	9.5	15.0	25.2							
600	E10	SCS	2.5	7.8	15.7	34.0	1.7						
	E10	HTA	7.2	9.5	16.2	37.6	2.3						
	EM102	SCS	7.5	8.7	17.0	34.2							
	EM102	HTA	7.0	9.9	16.4	34.3	2.5						
	DMH	HTS	77.2	3.7	7.3								

^a Dowmetal H = Mg + 6 per cent Al + 3 per cent Zn + 0.18 per cent Mn; HTS = 500 - 730°F. in 2 hr. + 730°F. (16 hr.) + 500°F. (4 hr.).

^b 1000 lb. per sq. inch.

^c S_p Plain specimen. S_n Notched specimen; stress concentration factor = 2. N.F. Notch factor = S_n/S_p.

^d Fatigue properties at 275°F.

cent Ce. Heat-treatment and aging also enhances the fatigue properties.

The changes in the conductivity of these alloys produced by the various heat-treatments are shown by the data in Table 6, together with the results for the manganese-containing alloys. These results differ from those presented in Table 2 in that the bars were air-cooled from the solution-heat-treating temperature as well

as from the aging temperature. Furthermore, the data presented here are for the standard compositions of alloys as considered for commercial applications.

Properties of Magnesium-cerium-manganese Alloys

Alloys containing various amounts of cerium with a nominal manganese content of 2 per cent have been investigated more

extensively than the plain magnesium-cerium alloys. Figs. 16, 17, and 18 show the mechanical and physical properties of alloys containing 1.4 to 1.7 per cent Mn

content; the effect is more pronounced at elevated temperatures. The tensile strength is not shown for temperatures below 450°F. because it increased some-

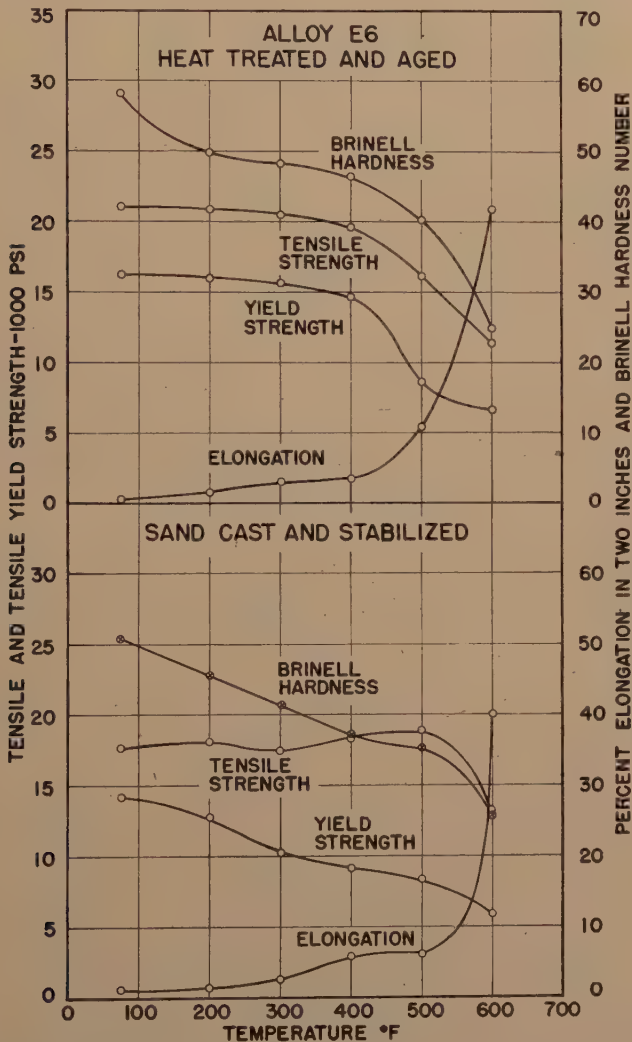


FIG. 14.—EFFECT OF TEMPERATURE ON PROPERTIES OF ALLOY E6, SAND-CAST.

as a function of cerium content in the range of 0.5 to 1.7 per cent at several temperatures. The alloys were all tested in the SCS condition. The strength properties show a marked increase with increasing cerium

what irregularly with increasing amounts of cerium at the lower temperatures; however, the Brinell hardness at room temperature increases uniformly with cerium content. As in the manganese-

free alloys, the elongation decreases markedly with increasing amounts of cerium.

The density (Fig. 18) increases linearly

effect of the stabilizing treatment is more pronounced at compositions below 4 per cent Ce. This is in agreement with the metallographic observation that the eutec-

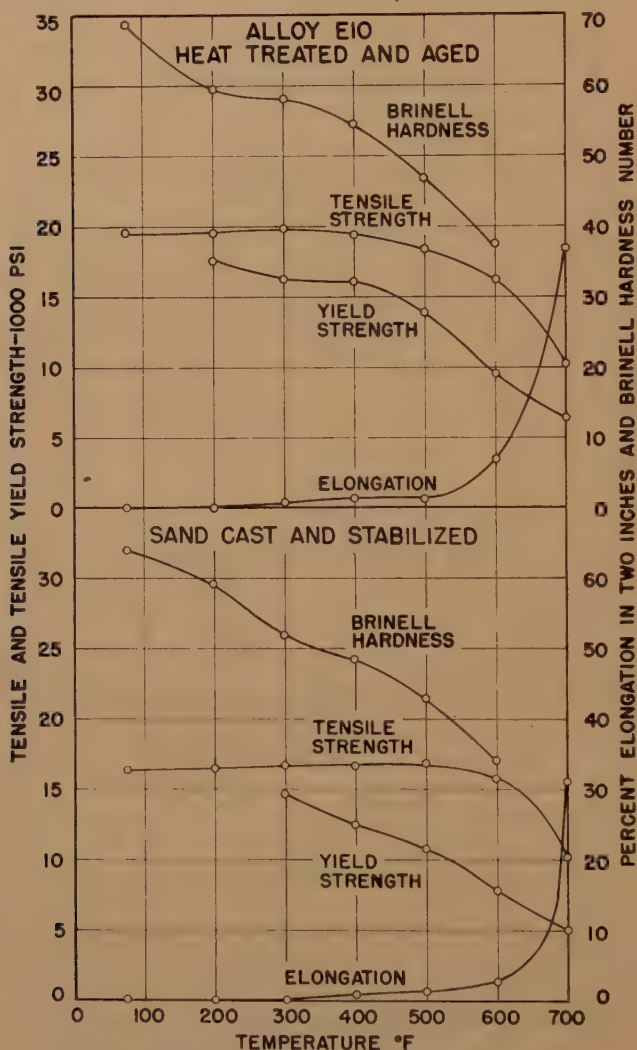


FIG. 15.—EFFECT OF TEMPERATURE ON PROPERTIES OF ALLOY E10, SAND-CAST.

with cerium content up to 12 per cent; beyond that, there is a slight deviation toward a higher value. Fig. 18 also shows the change in thermal and electrical conductivities both in the as-cast and the SCS conditions. It is of interest to note that the

tic network becomes continuous at that composition, thus rendering the alloys less sensitive to changes in the matrix.

Alloys containing 6 and 10 per cent Ce with 2 per cent Mn, EM62 and EM102, respectively, have been investigated more

thoroughly since they appeared the most promising. Figs. 19 and 20 show the variation in the mechanical properties of these alloys as a function of temperature.

cerium content from 6 to 10 per cent results in higher strength and hardness, and slightly lower ductility over the entire temperature range. The effect of heat-

TABLE 6.—*Electrical and Thermal Conductivity of Magnesium-cerium and Magnesium-cerium-manganese Alloys Compared with Dowmetal Alloys*

Alloy	Conductivity ^d at 20°C. (68°F.)									
	As Cast		SCS		HT		HTA		HTS	
	σ	K	σ	K	σ	K	σ	K	σ	K
E6.....	0.156	0.257	0.172	0.282	0.142	0.236	0.166	0.276	0.175	0.287
E10.....	0.132	0.221	0.148	0.246	0.116	0.197	0.135	0.226	0.143	0.238
EM62.....	0.116	0.197	0.155	0.256	0.123	0.208	0.136	0.227	0.171	0.280
EM102.....	0.107	0.183	0.142	0.236	0.104	0.179	0.116	0.197	0.145	0.241
Dowmetal H ^a	0.082	0.146			0.069	0.126	0.094	0.164	0.080	0.143
Dowmetal M ^b					(Extruded): $\sigma = 0.197$; $K = 0.320$					
Dowmetal O-1 ^c					(Forged HTA): $\sigma = 0.084$; $K = 0.150$					

^a Dowmetal H = Mg + 6 per cent Al + 3 per cent Zn + 0.18 per cent Mn; HT = 500 – 730°F. in 2 hr. + 730°F. (16 hr.); HTA = HT + 400°F. (16 hr.); HTS = HT + 500°F. (4 hr.). Electrical conductivity corrected to 20°C. using value of temperature coefficient of 0.0012 from Beck.¹

^b Dowmetal M = Mg + 1.5 per cent Mn. Electrical conductivity corrected to 20°C. using temperature coefficient for pure magnesium.

^c Dowmetal O-1 = Mg + 8.5 per cent Al + 0.7 per cent Zn + 0.15 per cent Mn; HTA = 760°F. (2 hr.) + 350°F. (24 hr.). Electrical conductivity corrected to 20°C. using value of temperature coefficient of 0.0092 from Beck.¹

^d σ = electrical conductivity in reciprocal microhm-centimeters. K = thermal conductivity in c.g.s. units.

TABLE 7.—*Comparison of Properties of Forged Magnesium-cerium-manganese Alloys with Wrought Dowmetal Alloys at Room Temperature and 300°F.*

Tem- pera- ture, Deg. F.	Alloy	Condition	Tensile Properties			Creep Limit ^b	Fatigue Properties ^{a,d} 1000 Lb. per Sq. In. to Indicated Life					
			Elong- ation, Per Cent	Yield Str. ^b	Ten- sile Str. ^b		10 ⁶ Cycles			10 ⁸ Cycles		
							S _p	S _n	N.F.	S _p	S _n	N.F.
Room	EMO2	Forged	9.8	25.3	36.8		16.0	10.0	0.63	11.0	5.5	0.50
	EM22	Forged	11.5	26.0	36.4		19.5	10.5	0.54	14.5	7.0	0.48
	EM42	Forged	8.0	27.1	37.0		18.0	11.5	0.63	15.5	6.0	0.39
	DM M ^a	Extruded	7.6	30.9	39.6	16.5	15.5	11.0	0.71	10.5	5.5	0.52
300 ^d	DM O-1 ^a	Forged HTA	4.5	39.5	52.9	22.0	26.0	14.5	0.56	16.0	9.5	0.59
	EM O2	Forged	24.5	19.5	23.2	18.0						
	EM22	Forged	19.0	20.6	25.4	21.0	16.5			12.0		
	EM42	Forged	13.8	21.5	27.2	21.0	19.0	10.0	0.53	16.0	4.0	0.25
	DM M	Extruded	15.7	18.7	21.3	8.7	12.5	9.0	0.72	8.5	4.5	0.53
	DM O-1	Forged HTA	30.3	20.7	31.0	2.8	20.5	10.5	0.51	10.5	5.0	0.48

^a Dowmetal M = Mg + 1.5 per cent Mn. Dowmetal O-1 = Mg + 8.5 per cent Al + 0.7 per cent Zn + 0.15 per cent Mn; HTA = 760°F. (2 hr.) + 350°F. (24 hr.).

^b 1000 lb. per sq. inch.

^c For notation, see Table 5.

^d Fatigue properties at 275°F.

These curves show the same general characteristics as the curves for the corresponding manganese-free alloys: (1) retention of high hardness and strength over a wide temperature range and (2) increasing the

treatment is further illustrated by the data included in Table 4 with that of the plain magnesium-cerium alloys. The effect of aging on the yield is slightly greater in the manganese-containing alloys than

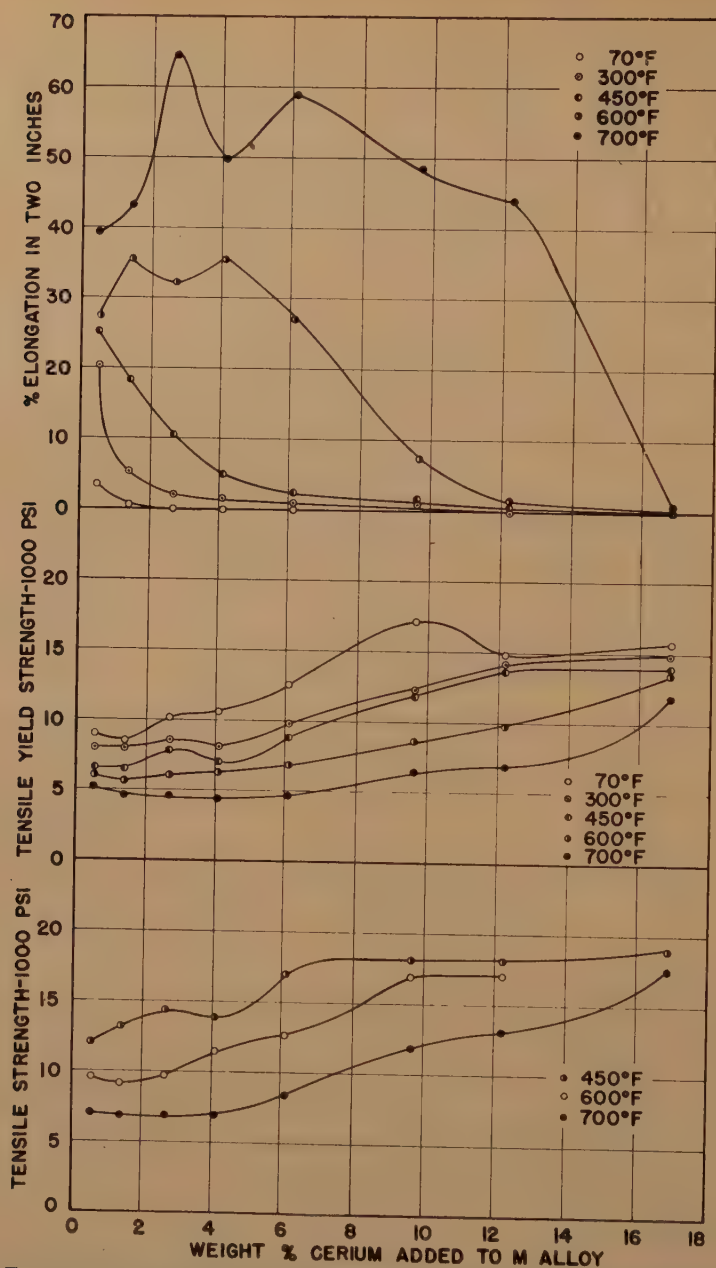


FIG. 16.—EFFECT OF CERIUM CONTENT ON TENSILE PROPERTIES OF M ALLOY, SCS CONDITION.

for the corresponding magnesium-cerium alloy. Stabilizing subsequent to heat-treatment results in about the same decrease in both strength properties and hardness as for the manganese-free alloys.

cerium alloys in Table 6. The addition of manganese results in a slightly lower conductivity in each case for all heat-treated conditions except the HTS. However, stabilizing at 600°F. subsequent to heat-

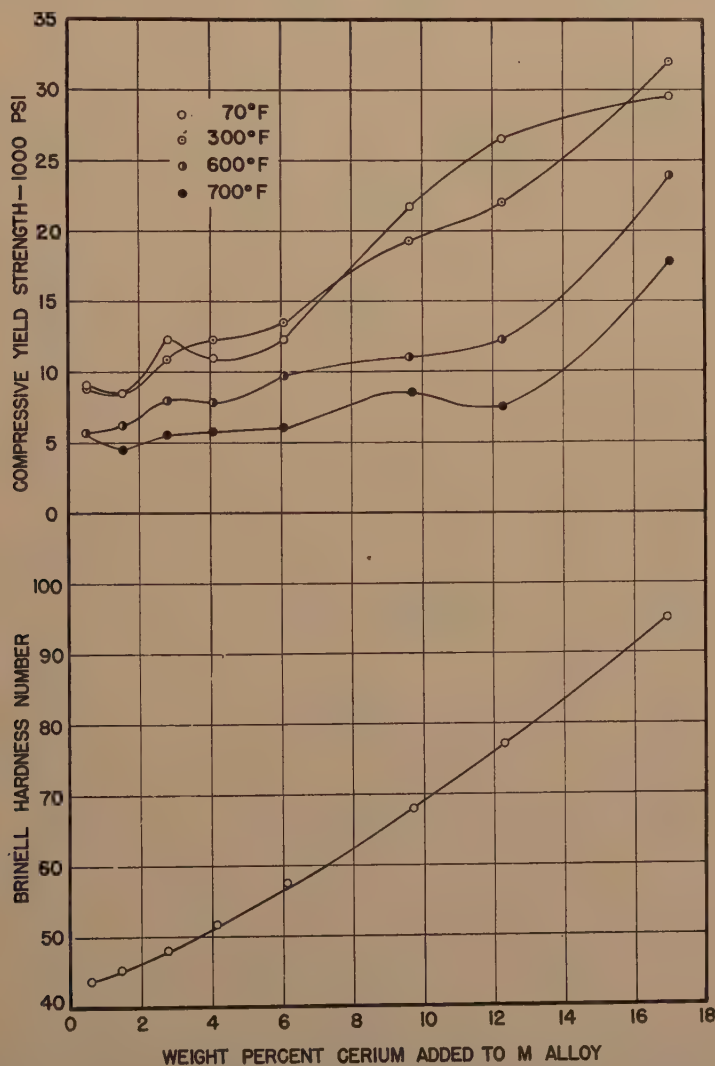


FIG. 17.—EFFECT OF CERIUM CONTENT ON COMPRESSIVE YIELD STRENGTH AND BRINELL HARDNESS OF M ALLOY, SCS CONDITION.

The effect of heat-treatment on the electrical and thermal conductivities of these alloys is compared with the corresponding properties of the magnesium-

treatments raises the conductivity of magnesium-cerium-manganese alloys to essentially the same value as the corresponding magnesium-cerium alloy, thus

indicating that the lower conductivity in the other conditions is due to an increase in solid solubility at the heat-treating temperatures.

The creep properties of these alloys

The results of rotating-beam fatigue tests, Table 5, again show the beneficial effect of heat-treatment. The fatigue properties of alloy EM62 are higher than those of alloy E6.

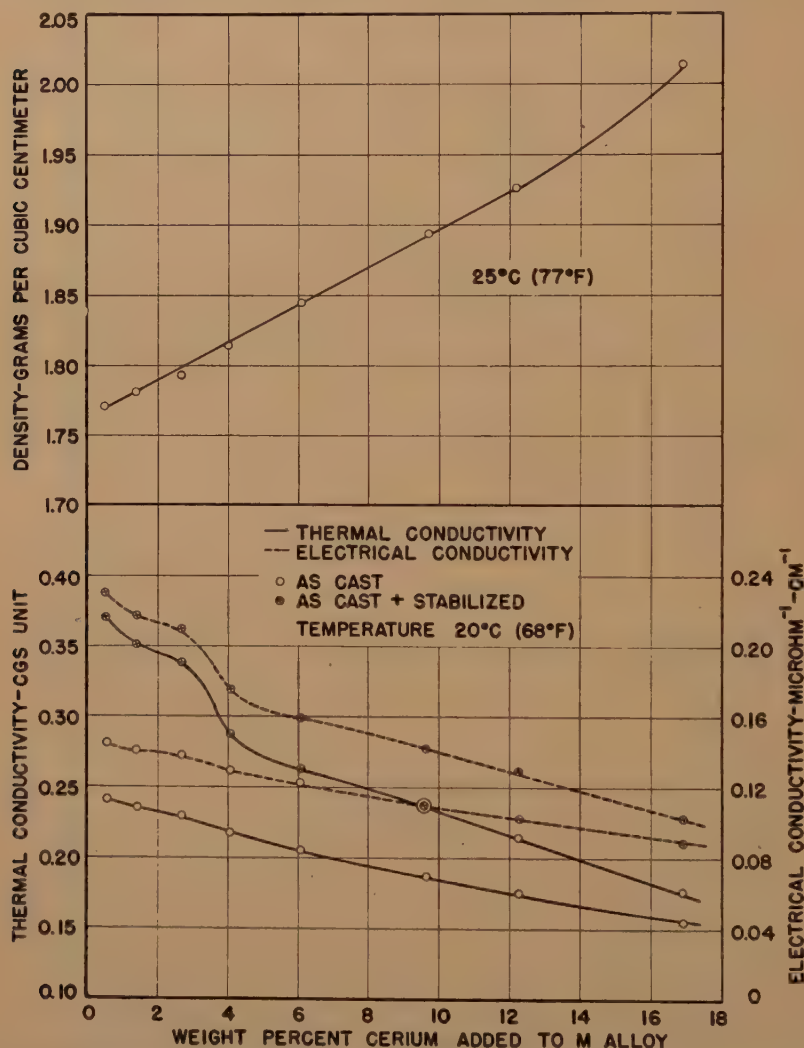


FIG. 18.—EFFECT OF CERIUM CONTENT ON DENSITY AND CONDUCTIVITY OF M ALLOY.

are included in Table 5. The presence of manganese in both the 6 and 10 per cent Ce alloys results in a slightly higher value in the creep limit over the entire temperature range investigated.

Manganese has a very marked effect on the corrosion resistance of magnesium-cerium alloys. Fig. 21 shows the change of corrosion rate of alloys containing 6 per cent Ce as a function of manganese con-

tent. Alloys containing less than 1.2 per cent Mn exhibit a very high rate of corrosion in 3 per cent NaCl solution, while an alloy containing 1.2 per cent Mn has a

PROPERTIES OF FORGED ALLOYS

Three magnesium alloys containing cerium and manganese have been in-

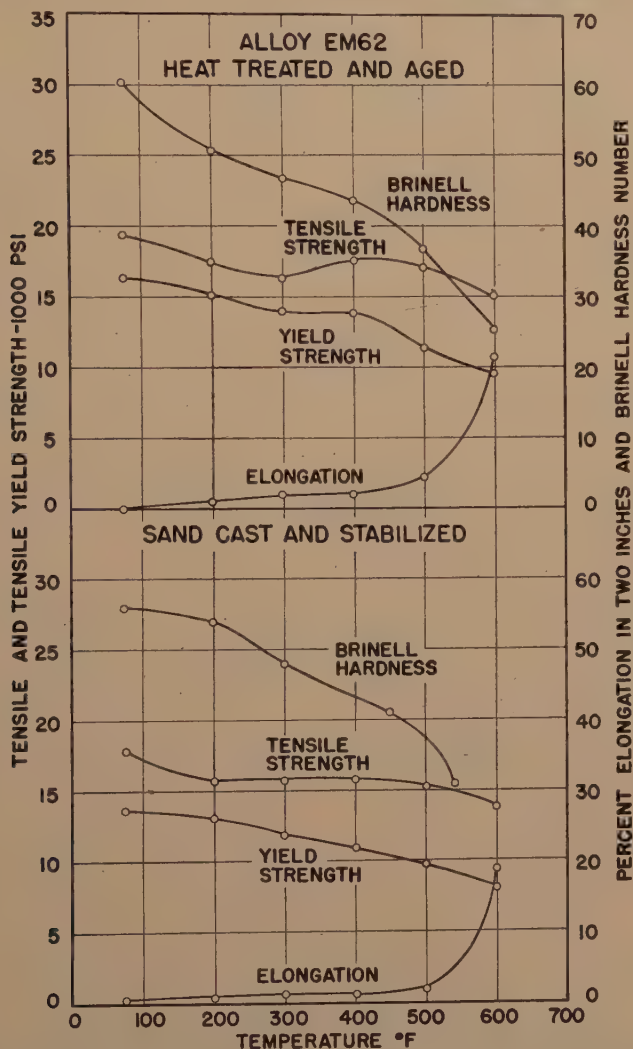


FIG. 19.—EFFECT OF TEMPERATURE ON PROPERTIES OF ALLOY EM62, SAND-CAST.

markedly reduced corrosion rate and a further improvement is obtained by increasing the manganese to 1.5 per cent. Corrosion tests of alloys containing 10 per cent Ce with and without manganese yield the same results as the corresponding 6 per cent Ce alloys.

vestigated in the forged condition. For these tests, bars were cut in the longitudinal direction from slabs $\frac{3}{4}$ in. thick. The slabs were forged sidewise from slugs of $2\frac{3}{4}$ -in. diameter, which had been extruded from cast billets of 8-in. diameter. Forging was carried out with the billet

stock at 1000°F. and the finishing temperature was 750°F.

The results of tension, creep, and fatigue tests at room temperature and at 300°F.

there is a slight increase in strength and a corresponding decrease in ductility with increasing cerium content. Alloy EM22 and EM42 have the same creep limit at 300°F.

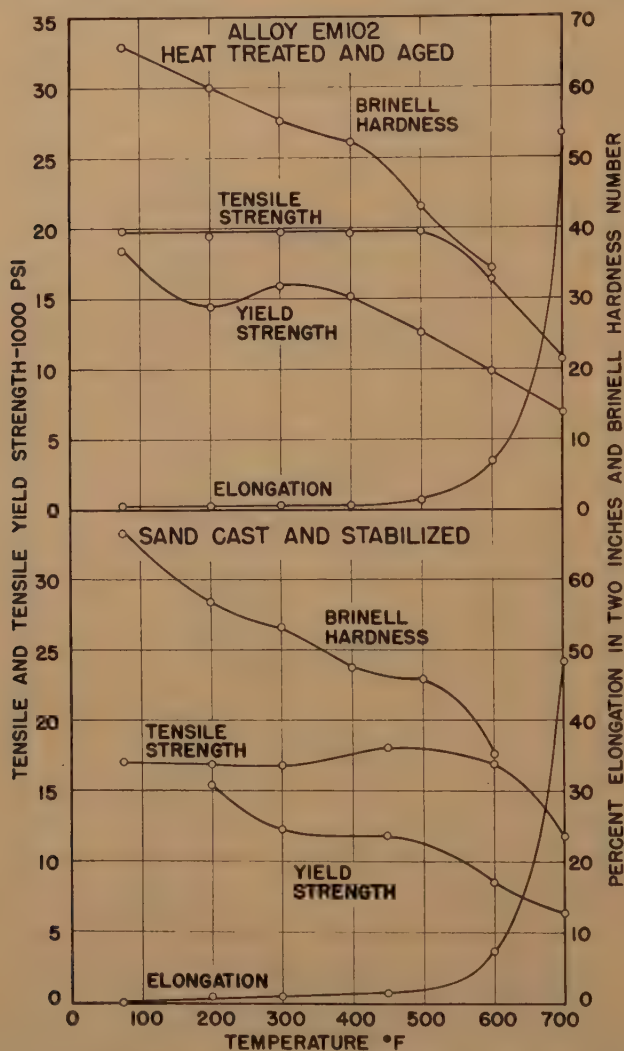


FIG. 20.—EFFECT OF TEMPERATURE ON PROPERTIES OF ALLOY EM102, SAND-CAST.

are summarized in Table 7. The tensile properties of the three alloys EM02, EM22, and EM42, containing 0.5, 2, and 4 per cent Ce, respectively, and all having a manganese content of 2 per cent, are very similar at room temperature but at 300°F.

and are only slightly superior to the alloy with the lowest cerium content. EM02. At 400°F., both alloy EM22 and EM42 have a creep limit of 6500 lb. per sq. in. The creep resistance of the alloys containing 2 and 4 per cent Ce at 300°F. is superior to

any of the cast alloys discussed in the preceding paragraphs. There is very little difference between the fatigue properties of the three alloys.

which decreases with increasing aluminum content.

In the present work, the properties of alloy EM62 have been studied as a function

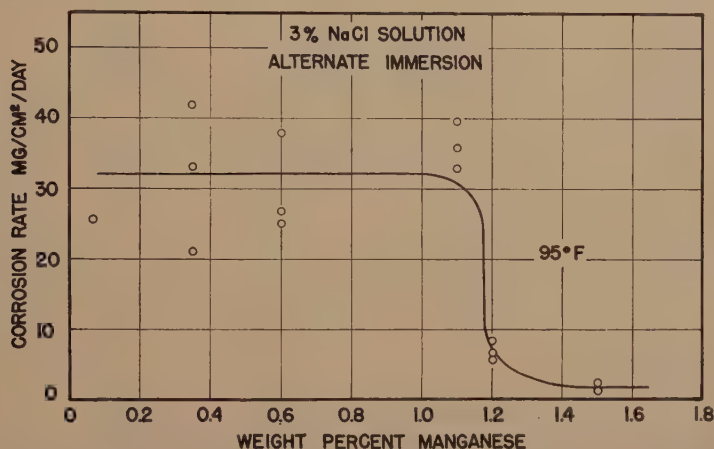


FIG. 21.—EFFECT OF MANGANESE CONTENT ON CORROSION RATE OF ALLOY CONTAINING MAGNESIUM PLUS 6 PER CENT CERIUM.

EFFECT OF ALUMINUM ON PROPERTIES OF ALLOY EM62

The constitution of magnesium-aluminum-cerium alloys has been investigated by Pogodin and Mikheeva⁹ within the Mg-Mg₉Ce-Mg₁₇Al₁₂ triangle of the ternary diagram. It was observed by these investigators that aluminum decreases the solid solubility of cerium in magnesium to very low values and effects marked changes in the microstructure. Mäder and Laves¹⁰ have shown that additions of aluminum to the German alloy AM537 (1.5 per cent Mn + 0.5 per cent Ce) decrease both the strength and ductility of rolled sheet. Furthermore, in alloys containing 1 per cent Al, the Mg₉Ce grain-boundary network occurring in the bead and the fusion zone of welded structures of this alloy is replaced by small particles of CeAl₂ distributed in the grain boundaries. In alloys containing less than one per cent aluminum, the CeAl₂ phase is associated with the Mg₉Ce compound, the amount of

aluminum content up to 2.5 per cent Al. The composition of the alloys is given in Table 8. The cerium content was held between 4.2 and 5.8 per cent, while the manganese decreased to as low as 0.63 per

TABLE 8.—Composition of Aluminum-containing EM62 Alloys PER CENT

Nominal Aluminum Addition	Ce	Mn	Al
0	6.27	1.8	0
0.20	4.7	1.7	0.20
0.40	4.3	1.3	0.36
0.80	5.0	0.93	0.83
1.00	5.8	0.95	1.00
1.50	5.6	1.1	1.40
1.80	4.8	0.77	1.80
2.00	4.2	0.63	2.10
2.50	5.1	0.95	2.50

cent at the higher aluminum contents, because of the relatively low solubility of manganese in molten magnesium when aluminum is present.

The effect of aluminum on the tensile properties of alloy EM62 is shown in Fig.

22. The tensile strength is not materially affected at 70° and 300°F., but at 600°F. it falls off markedly with increasing aluminum content. The yield strength decreases

properties are not a result of the lower cerium content, as can be seen by comparing these properties with those of an alloy containing an equivalent amount of cerium.

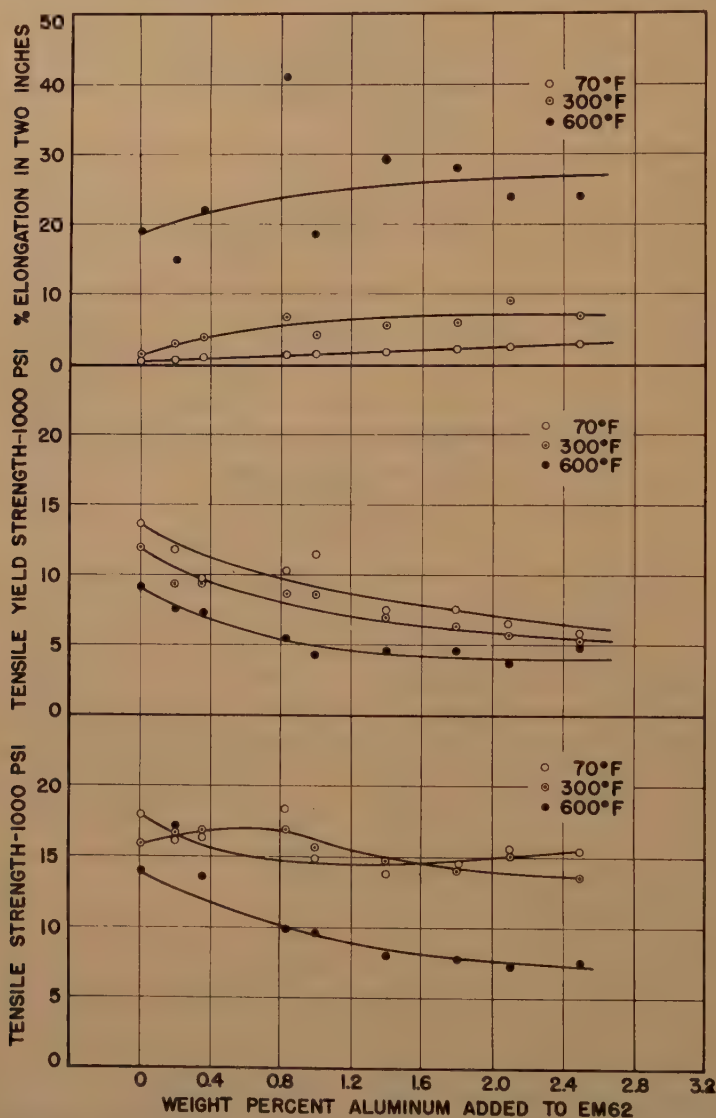


FIG. 22.—EFFECT OF ALUMINUM CONTENT ON TENSILE PROPERTIES OF ALLOY EM62, SCS CONDITION.

continuously with increasing amounts of aluminum and the elongation increases at all temperatures. The changes in the tensile

Fig. 23 shows the change in electrical and thermal conductivity as a function of aluminum content in the as-cast and the SCS

conditions. The conductivity increases with aluminum to a maximum value at 1.8 per cent Al. The stabilizing treatment results in the usual increase in conductivity

the alloys except that containing 2.5 per cent Al. The observed structures of these alloys are similar to those shown by Pogodin and Mikheeva. Thus, the increase in the

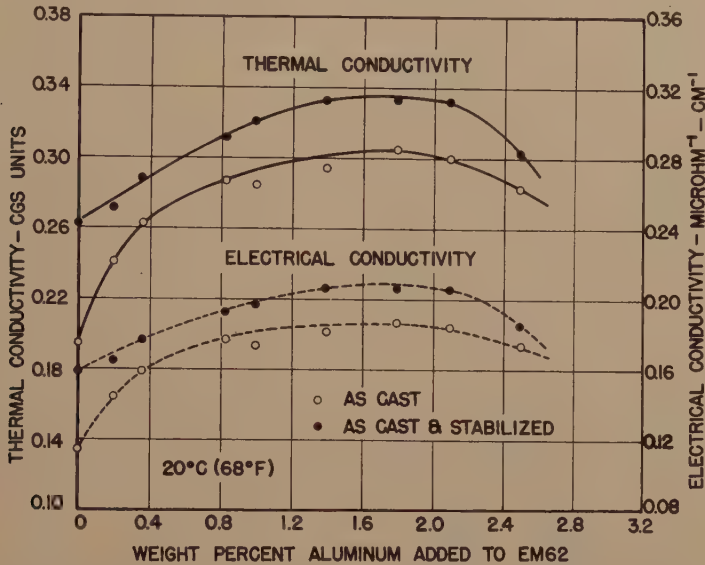


FIG. 23.—EFFECT OF ALUMINUM CONTENT ON CONDUCTIVITY OF ALLOY EM62, SAND-CAST.

due to the depletion of solute in the matrix by precipitation.

The changes in the microstructure of alloy EM62 as a result of the additions of aluminum are shown by the series of micrographs in Figs. 24 and 25. With 0.20 per cent Al the structure is not very different from that of EM62 except that there are traces of a new phase present within the Mg_9Ce phase, while in the alloy containing 0.36 per cent Al this new phase appears throughout the eutectic network. A "Chinese script" type of eutectic appears at 0.83 per cent Al. The amount of this eutectic increases and that of Mg_9Ce decreases with increasing aluminum content until at 2.5 per cent Al there is no Mg_9Ce present and the new eutectic forms a continuous network. The alloys containing 0.83 to 2.1 per cent Al have a Widmanstätten precipitate in the as-cast structure. Stabilizing at 600°F. produces a coarse precipitate throughout the matrix in all

conductivity resulting from the addition of aluminum to alloy EM62 must be associated with: (1) the decrease in solid solubility of cerium, and (2) the replacement of the Mg_9Ce network by the new type of eutectic observed in the higher aluminum contents.

DISCUSSION OF RESULTS

The results of this investigation have shown that the addition of cerium to magnesium produces alloys that retain much of their strength at elevated temperatures and exhibit high resistance to creep over a wide range of temperatures. The data have been discussed in full in the preceding sections.

In conclusion, a few remarks may be made in the way of a comparison between the alloys discussed in this paper and some of the presently used commercial magnesium alloys.

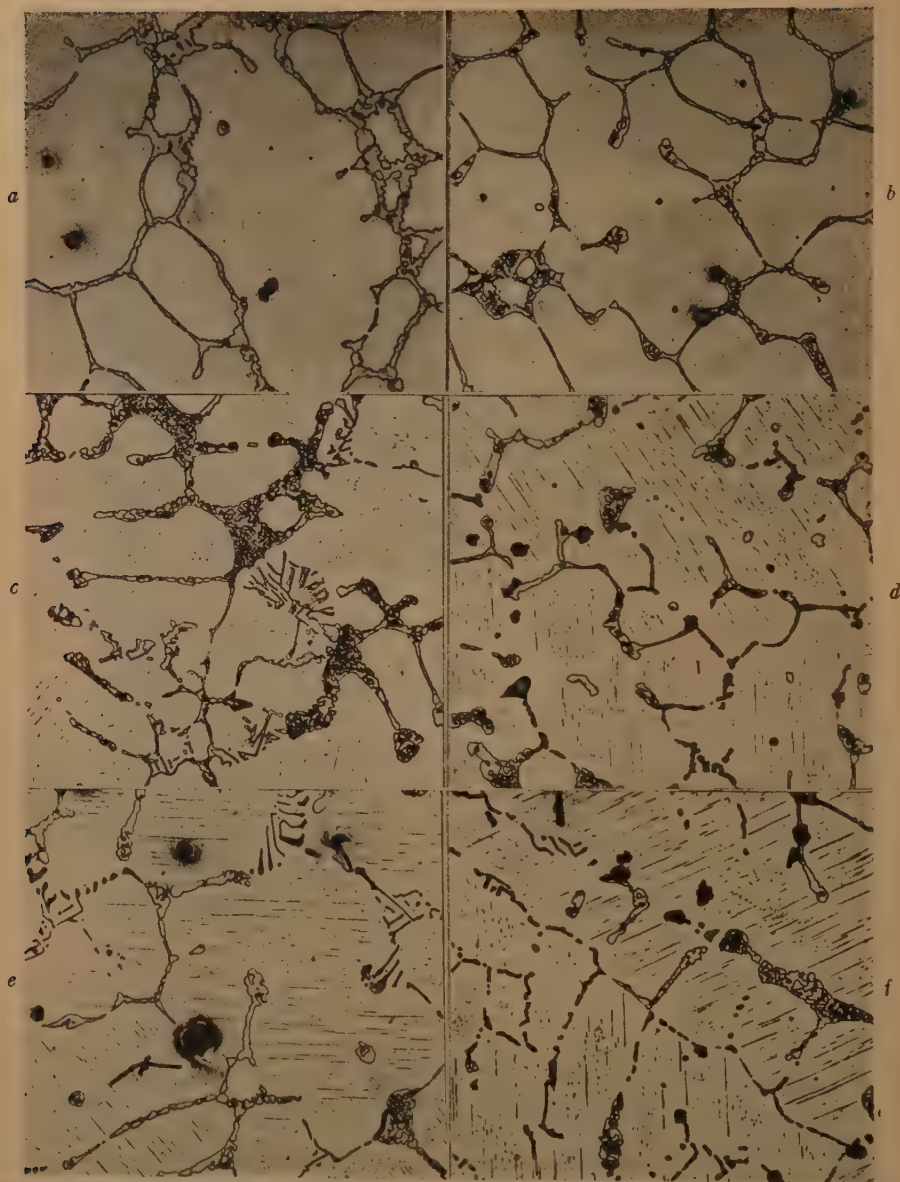


FIG. 24.—MICROSTRUCTURE OF SAND-CAST ALLOY EM62 CONTAINING VARIOUS AMOUNTS OF ALUMINUM IN THE AS-CAST CONDITION. $\times 250$.
a. 0.20 per cent Al. *b.* 0.36 per cent Al. *c.* 0.83 per cent Al. *d.* 1.00 per cent Al. *e.* 1.40 per cent Al. *f.* 1.80 per cent Al.

The properties of Dowmetal H (Mg + 6 per cent Al + 3 per cent Zn + 0.18 per cent Mn) are included in Table 5 with the corresponding properties of the cerium-containing magnesium alloys. On the basis

of the tensile yield strength, the alloys containing 10 per cent Ce and 10 per cent Ce plus 2 per cent Mn in the HTA condition are superior to H alloy in the HTS condition over the entire temperature

range from 70° to 600°F. , while the alloys containing 6 per cent Ce, with and without manganese, have comparable values at temperatures up to 300°F. , and above that they become increasingly better than H alloy with increasing temperature. The tensile strength of alloys containing cerium is somewhat lower than that of Dowmetal H at room temperature and at 300°F. , but at temperatures above 300°F. the former alloys are superior to H alloy and their superiority increases with increasing temperature.

In a word, it may be said that the distinguishing feature of the cerium-containing magnesium alloys is their retention of high strength at elevated temperatures in contrast to the decrease in strength of Dowmetal H at temperatures above 300°F. This is further emphasized by the markedly high resistance to creep of these alloy at elevated temperatures and the proportionately smaller decrease in fatigue resistance with increasing temperature than is exhibited by H alloy. The creep limit values of the cerium-containing alloys at 300°F. are all very high compared with their static properties, while in Dowmetal H the creep limit has decreased from 20,700 lb. per sq. in. at room temperature to 4300 lb. per sq. in. at 300°F. , as compared with a yield strength of 14,000 lb. per sq. in. at that temperature. Direct comparison cannot be made at any other temperature because of the incompleteness of the data, but it is apparent that H alloy will exhibit poor resistance to creep at temperatures above 300°F. compared with the cerium-containing alloys.

The properties of forged magnesium-cerium-manganese alloys are compared with extruded Dowmetal M (Mg + 1.5 per cent Mn) and with forged Dowmetal O-1 (Mg + 8.5 per cent Al + 0.7 per cent Zn + 0.15 per cent Mn) in Table 7. The same general features are exhibited by the forged cerium-containing alloys as have been discussed for the cast alloys. While the tensile properties of the magnesium-cerium-manganese alloys are some-

what lower at room temperature than those of the high-strength alloy, Dowmetal O-1, the latter alloy suffers a proportionately greater decrease in strength with

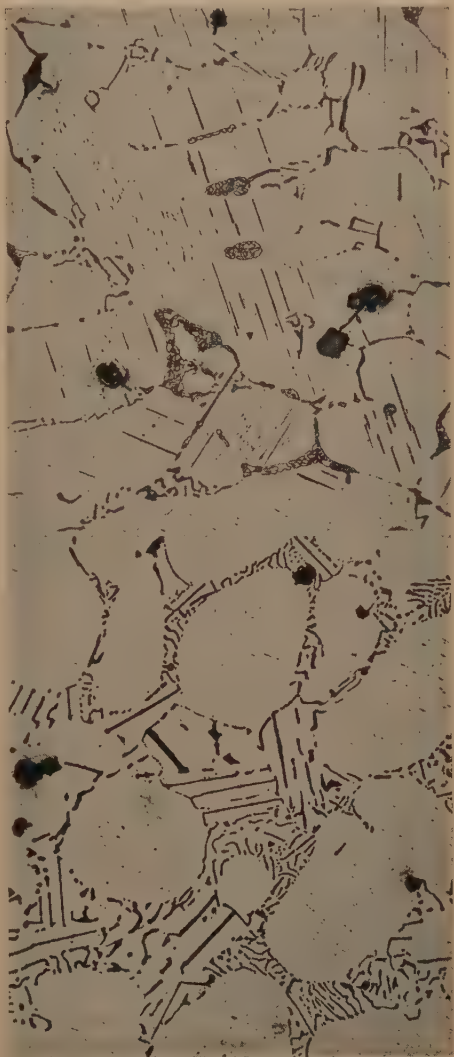


FIG. 25.—MICROSTRUCTURE OF SAND-CAST ALLOY EM62 CONTAINING: *a* 2.1 PER CENT ALUMINUM AND *b* 2.5 PER CENT ALUMINUM. AS-CAST. $\times 250$.

increasing temperature so that at 300°F. the cerium alloys are comparable to it on the basis of yield strength and only slightly inferior in tensile strength. In comparison with extruded Dowmetal M, the cerium-

containing alloys have comparable tensile properties at room temperature and are definitely superior to this alloy at 300°F. On the basis of creep resistance, the cerium-containing alloys are markedly superior to either of the commercial alloys at 300°F. The creep limit of Dowmetal O-1 is strongly affected by increasing temperature while extruded Dowmetal M shows the highest resistance to temperature of any of the presently used commercial magnesium alloys, either cast or wrought. The latter effect is also illustrated by the fatigue properties.

Comparison of the conductivity of the cerium-containing magnesium alloys with that of the commercial magnesium alloys is made in Table 6. All the alloys containing cerium have markedly higher conductivity values than either Dowmetal H or Dowmetal O-1; the differences are more pronounced in the stabilized conditions. Dowmetal M has a slightly higher conductivity than the magnesium-cerium alloys. H alloy in the HTS condition has a lower conductivity than in the HTA condition, indicating that stabilizing at 500°F. does not cause the same degree of precipitation as aging at 400°F. for 16 hours.

SUMMARY

1. The properties of magnesium alloys containing various amounts of cerium have been determined at room and elevated temperatures.

2. Additions of cerium to magnesium produce alloys that retain relatively high strength and hardness at temperatures up to 400° or 500°F.

3. Increasing amounts of cerium increase the elevated-temperature strength and hardness of magnesium alloys.

4. The creep resistance of cerium-containing magnesium alloys is superior to that of other known magnesium alloys at elevated temperatures.

5. The properties of cerium-containing magnesium alloys are enhanced by heat-

treatment and aging. This effect is more pronounced in the case of the creep resistance at 300° and 400°F.

6. The elevated-temperature properties of magnesium-cerium alloys are improved somewhat by additions of manganese.

7. Additions of manganese greater than 1.1 per cent markedly improve the corrosion resistance of magnesium-cerium alloys in 3 per cent NaCl solution.

8. Manganese increases the solid solubility of cerium in magnesium at heat-treating temperatures.

9. The conductivity of cerium-containing magnesium alloys is markedly higher than any of the presently used commercial magnesium alloys, with the exception of Dowmetal M.

10. These alloys can be rendered dimensionally stable by proper aging following the solution heat-treatment.

11. Additions of aluminum to alloy EM62 decrease the strength properties at elevated temperatures and increase the ductility and conductivity.

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DISCUSSION

(J. D. Hanawalt presiding)

P. W. BAKARIAN.*—It is interesting to point out the comparison between the mag-

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nesium-cerium alloys as presented in this paper and some of the standard alloys in aluminum used at elevated temperatures. The alloy 142, or Y, is commonly used for such purposes in the aircraft industry where high tensile strength is required and a range up to 600°F. is reached. The tensile strength in these magnesium-cerium alloys averages about 15,000 lb. per sq. in. at 600°, whereas 142, or Y, at that temperature averages 9,000 to 12,000 lb. per sq. in. Thus it seems that advantage will be obtained by the use of the magnesium-cerium compositions in future developments where the temperature-strength properties are an important factor.

J. R. BURNS.*—How long were the alloys preheated before testing to obtain the properties shown in the slides?

T. E. LEONTIS.—As far as the properties that have been reported are concerned, the holding time was limited to 10 min. In other words, we have abbreviated the holding period from the one hour that is required by the A.S.T.M. specifications on the basis of previous studies on magnesium alloys that have shown no difference between 1 hr. and 10 min. However, I'd like to point out that we are considering the effect of extended holding times at high temperatures, and we have already instigated a program to study this problem, extending the time out to several thousands of hours.

L. W. KEMPF.†—Mr. Leontis made some reference to the effect of manganese on grain size. Another of the difficulties with these cerium-manganese alloys is the tendency for the development of large grain at slightly elevated pouring temperatures. As is well known, in the making of commercial castings, it is sometimes quite difficult to restrict pouring temperatures to the immediate vicinity of the liquidus, and alloys that develop coarse grains at slightly elevated pouring temperatures are at a distinct disadvantage. I wonder if Mr. Leontis would care to comment on these points?

T. E. LEONTIS.—The effects of both pouring temperature and manganese content on the grain size of magnesium-cerium alloys are discussed in the paper. It is quite true that increasing manganese content as well as increasing the pouring temperature increases the grain size. In casting commercial products, it becomes necessary to go to more elevated pouring temperatures. For that reason, we are at present working on methods of refining the size of magnesium-cerium-manganese alloys. As stated in the paper, one of the methods we have found is by the addition of zirconium. However, there are difficulties with this method and we are also trying other methods in the direction of producing fine-grained magnesium-cerium-manganese alloys.

J. D. HANAWALT.*—I do not recall whether Mr. Leontis mentioned that in Germany the magnesium-cerium alloy was in commercial use. I had the opportunity to investigate the German magnesium industry last summer. As far as I know, the use of cerium in commercial magnesium articles is the only element the Germans were using in magnesium-base alloys that was not used in this country at the start of the war.

For instance, the German BMW aircraft engine used magnesium-cerium alloys as forgings on the supercharger impeller and the rear cam-follower guide. I believe it would be, in dimension, about 24 in. in diameter. Later, during the war, when their source of cerium was no longer available, they changed that forging to a magnesium-base aluminum-zinc alloy, which is quite common in this country.

It occurs to me that it is pertinent at this meeting to mention the designation of the alloys we have heard about this morning. It would be quite a help if we all knew that system.

These alloys were frequently called EM62, and we have heard a good deal of AZ31, and so on. The system simply is to use the letter *A* for aluminum, *Z* for zinc, *M* for manganese, *C* for calcium and *E* for cerium. So that, for instance, if we have 3 aluminum, 1 zinc, it is AZ31. If we have 6 cerium, 2 manganese, it is EM62, and so on. It is very simple and can be helpful to have such a system.

* Wright Field, Dayton, Ohio.

† Aluminum Company of America, Cleveland, Ohio.

* Director of Metallurgical Department, The Dow Chemical Co., Midland, Michigan.

Susceptibility of Four Magnesium Casting Alloys to Microporosity and Its Effect on the Mechanical Properties

By JAY R. BURNS,* JUNIOR MEMBER A.I.M.E.

(Chicago Meeting, February 1946)

Two magnesium sand-casting alloys are commonly favored in the United States. These are referred to as H and C alloys (Dow Chemical Co.) or AM265 and AM260 alloys (American Magnesium Corporation). Both are of an aluminum-zinc-manganese type. H alloy contains 6 per cent aluminum and 3 per cent zinc and is characterized by relatively good toughness. C alloy contains 9 per cent aluminum and 2 per cent zinc and is employed where high yield strength and pressure tightness are required.

Examination of magnesium castings poured in Europe and England,^{1,2} however, demonstrates that H and C alloys are replaced by A8 and AZ91, respectively. That is, A8 represents a magnesium alloy having superior toughness while AZ91 is suitable for high yield strength and pressure-tight applications.

The basic difference between the American and European alloys is that the foreign alloys employ a somewhat higher aluminum content and less zinc than is found in H and C alloys. The mechanical properties of the alloys, when divided into high and low-aluminum groups, are quite similar, as determined from separately cast foundry-control type test bars.³

In this paper the decrease of mechanical

properties caused by any given amount of microporosity is measured for H, C, A8, and AZ91 alloys. The relative susceptibility of each of the four alloys to microporosity is also determined.

Typical mechanical properties and nominal chemical analyses are reported in Table I.

TABLE I.—Composition and Typical Mechanical Properties of Magnesium Sand-casting Alloys⁴

Alloy	Composition, Per Cent			Ultimate Tensile Strength, Lb. per Sq. In.	Tensile Yield Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.
	Alum- inum	Zinc	Man- ganese			
Group 1. Low Aluminum, Superior Toughness						
H A8	6.0	3.0	0.20	38,600	14,200	12.0
	8.0	0.4	0.20	38,000	13,000	13.0
(Properties in solution-heat-treated condition)						
Group 2. High Aluminum, High Yield Strength						
C AZ91	9.0	2.0	0.20	39,900	24,800	2.0
	9.5	0.4	0.20	38,100	22,200	2.0
(Properties in solution-heat-treated and aged condition)						

The apparent similarities between the two alloys in each group have led to considerable discussion as to the relative merits of each of the compositions.² Popular points for comparison between the alloys have been the relative susceptibility of each of the four alloys to microporosity⁵ and the effect of this microporosity on their mechanical properties. It is primarily intended, in this paper, to show the

Manuscript received at the office of the Institute July 30, 1945. Issued as T.P. 1955 in METALS TECHNOLOGY, February 1946.

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¹ References are at the end of the paper.

effect of any given amount of microporosity on the mechanical properties of each of the four alloys. Sufficient data are also presented to provide an assessment of the

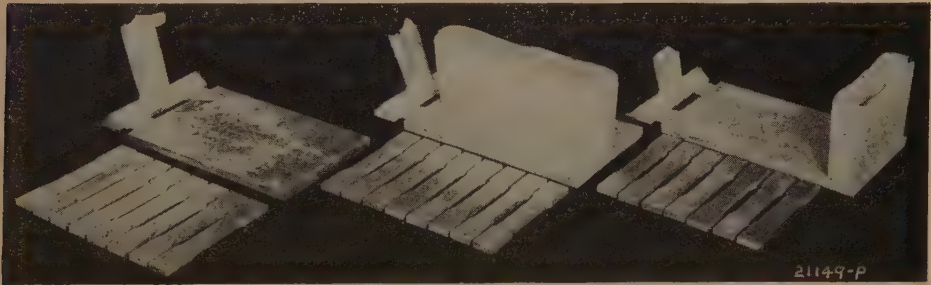
R. S. Busk⁶ has presented a method of quantitatively evaluating the severity of microporosity in test bars. This and several other procedures were investigated



Horizontal two-end risers

Horizontal, four risers

Vertical, small riser



Horizontal, no risers

Horizontal, riser over center

Horizontal, one end riser

FIG. 1.—SIX TYPES OF TEST CASTINGS.

characteristic susceptibility of each alloy to microporosity.

MATERIAL AND PROCEDURE

The test casting selected for the work was a 6 by 10 by $\frac{1}{2}$ -in. plate, gated and risered in six different ways, as shown in Fig. 1. In this manner, microporosity was controlled both as to quantity and distribution. Each of the castings was cut into test bars as shown in Fig. 1. The bars were flat to facilitate later radiographic work and had a 2 by 0.75 by 0.3-in. gauge length. Radiographs of typical bars from various test castings are shown in Fig. 2. The microporosity was varied from zero to a quantity considerably in excess of that found in commercial castings.

as possible techniques for measuring the microporosity present. The following method was developed as being the most desirable for this work insofar as scatter of results and elimination of "the human element" were concerned.

The test bars were radiographed at 44 kv. and 5 ma., using Eastman type-A film. Preformed lead shielding was placed on the sides of each bar. A small step block was included on every film, to check any change of gamma that might have occurred in development or from other cause. The film background—i.e., the image of the nonporous portions of the bars—was maintained between 1.0 and 1.2 density units. The greatest difficulty arose in attempting to maintain a uniform back-

ground density over the individual films. Constant stirring of the developer, together with film agitation, did much to ensure the necessary uniformity.

bar. The two density readings were then subtracted, the difference being proportional to the severity of porosity within the gauge length of the bar. This difference



FIG. 2.—RADIOGRAPHS OF TYPICAL TEST BARS.
I. From horizontal plate with no risers.
II. From horizontal plate with one end riser.
III. From horizontal plate with riser over center.
IV. From vertical plate with small riser.

Six bars were radiographed at one time on an 8 by 10-in. film. After the film had been processed in the dark room, it was checked for proper uniformity of density and, if satisfactory, cut into strips equal in width and coinciding with the images of the bars thereon. These strips were then slowly passed over the window of a photoelectric cell connected to a vacuum-tube amplifier and milliammeter (Fig. 3). The milliammeter was calibrated directly in density units. The cell opening was $\frac{1}{8}$ by $\frac{5}{8}$ in., the size having been determined after brief experimentation on the scatter of results obtained with openings of various sizes.

Two density readings were recorded during the scanning process—the minimum or background density, and the maximum density noted within the section of film encompassing the gauge length of the test

is referred to as the porosity index. The maximum severity of porosity occurred within the gauge lengths of the bars, with only few exceptions.

The mechanical properties of each test bar were determined and correlated with the porosity index. This was done for each alloy in the as-cast, solution-heat-treated, and solution-heat-treated and aged conditions. Approximately 70 bars were used in each of the 12 cases, all six types of castings being represented in each group of 70 bars. The results are plotted in Figs. 4 through 27. Each point represents the results obtained from a single test bar. Some bars contained small oxide inclusions at the fracture and are distinguished on the graphs by a "↑" point. A portion of the fractured tensile bars was compared with the radiographs to demon-

strate that fracture occurred at the location of the most severe microporosity.

RESULTS

Definite differences exist in the response

In Figs. 4 through 27, porosity indices less than 0.02 indicate no visible porosity, in most cases. The porosity index does not quite reach zero, probably because of segregation in the casting and unevenness

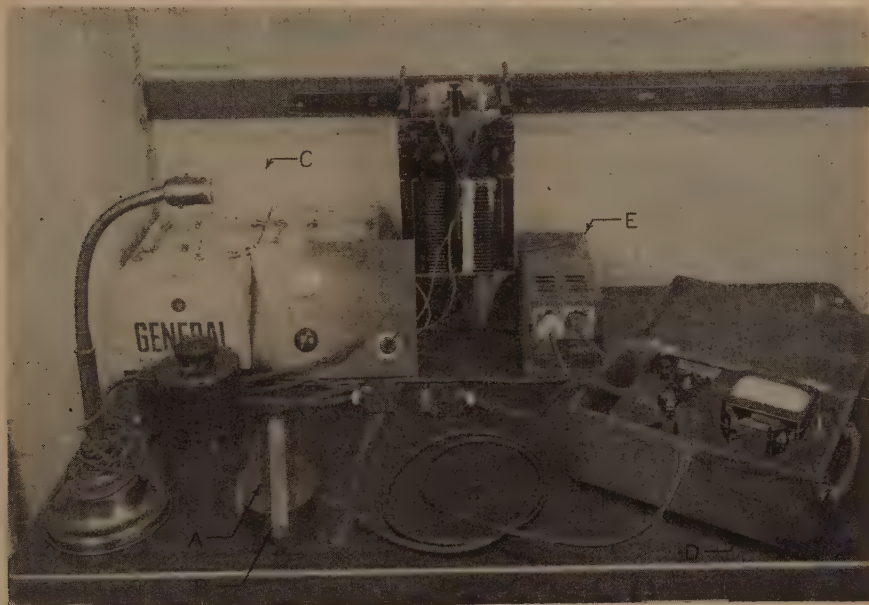


FIG. 3.—SCANNING APPARATUS.

- | | |
|------------------------------------|---|
| A. Window into photoelectric cell. | D. Amplifying and density measuring instrument. |
| B. Guide for films of test bars. | E. Voltage stabilizer for light source. |
| C. Light source. | |

of the various alloys to equivalent amounts of microporosity, as determined radiographically. As an example, if a porosity index of 0.1 is assumed, H alloy, solution-heat-treated, will possess an ultimate tensile strength figure of 20,750 lb. per sq. in., whereas A8 alloy will possess an ultimate tensile strength of 14,000 lb. per sq. in. in a similarly heat-treated condition. As shown in Table 1, the ultimate tensile-strengths of H and A8 alloys are similar when determined on sound bars. It may be stated, after a comparison of Figs. 4 through 27, that the presently used American alloys can tolerate a greater amount of microporosity and still retain their high mechanical properties than can the comparable European alloys.

of film development. The initial rapid diminution of ultimate tensile strength is probably due to the strong notch effect of the first few voids.

Grain diameters were measured on all melts poured and were found to be in the neighborhood of 0.006 inches.

SUSCEPTIBILITY TO MICROPOROSITY

Procedure

Only two of the six types of test castings (Fig. 1) are considered in this section. These consist of the horizontal castings having no risers and those having a riser over the center. These castings were sectioned into eight equally spaced parallel test bars numbered 1 through 8, No. 1 being at the gate end. The porosity indices

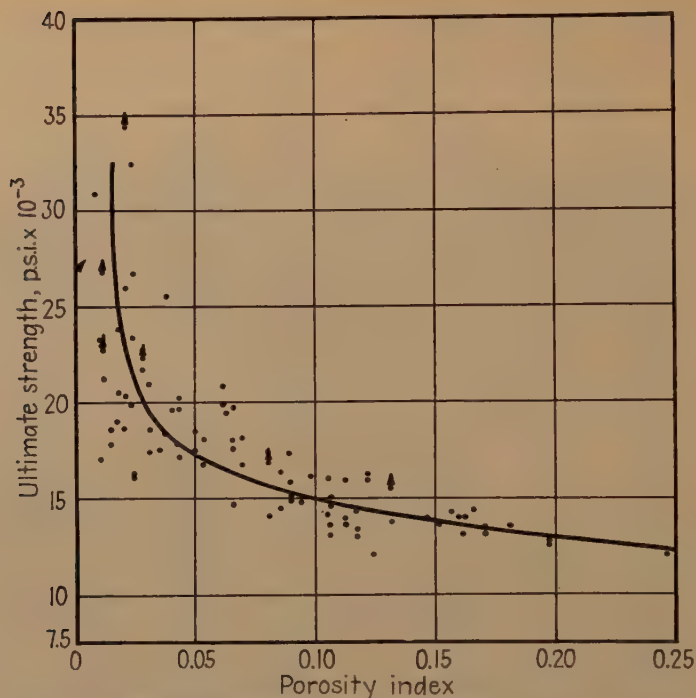


FIG. 4.—ULTIMATE STRENGTH VS. POROSITY INDEX, H ALLOY AS CAST.

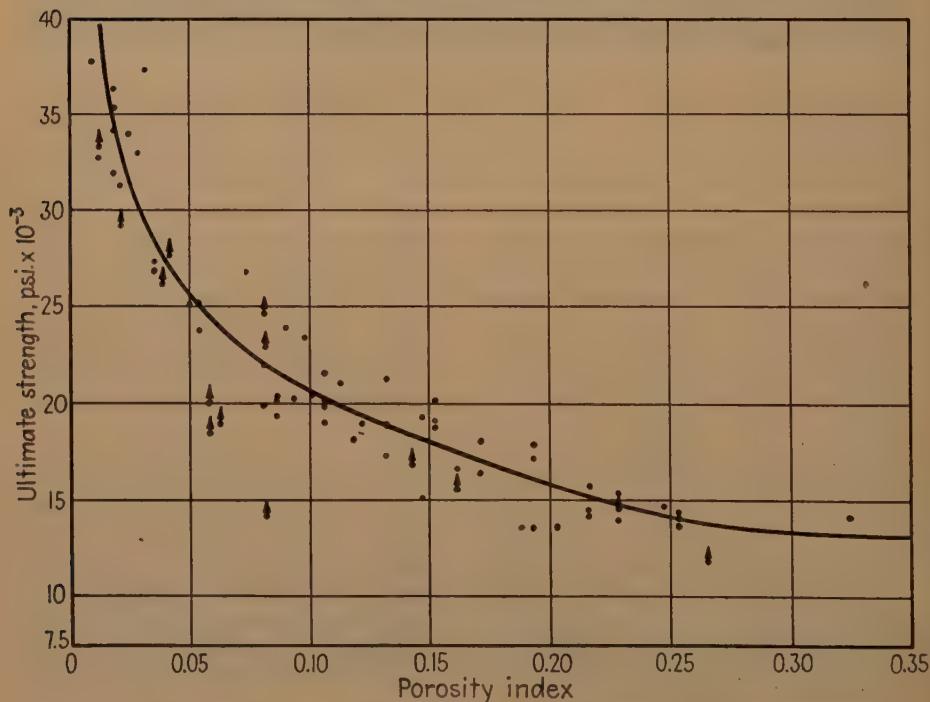


FIG. 5.—ULTIMATE STRENGTH VS. POROSITY INDEX, H ALLOY SOLUTION-HEAT-TREATED.

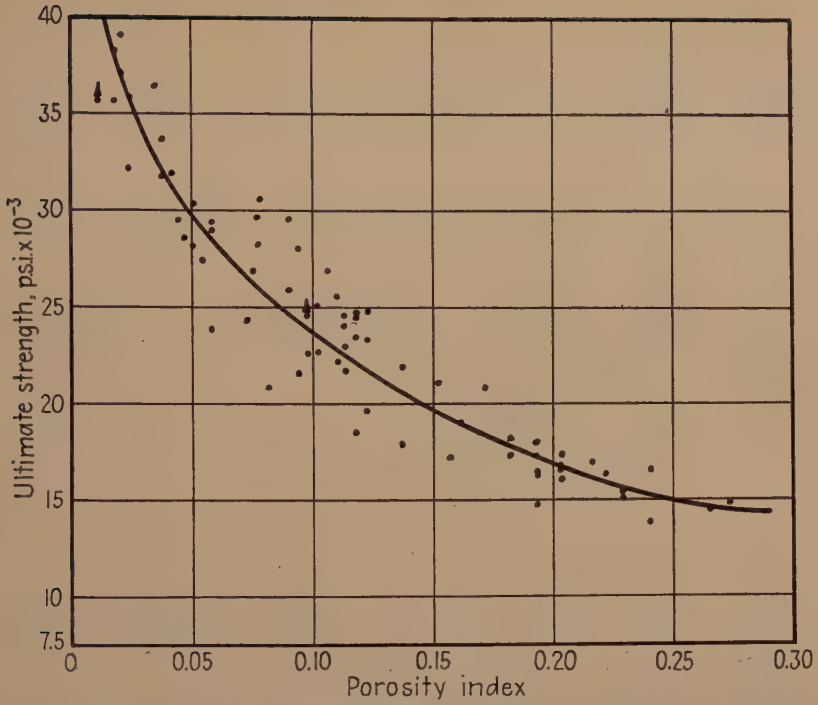


FIG. 6.—ULTIMATE STRENGTH VS. POROSITY INDEX, H ALLOY, SOLUTION-HEAT-TREATED AND AGED.

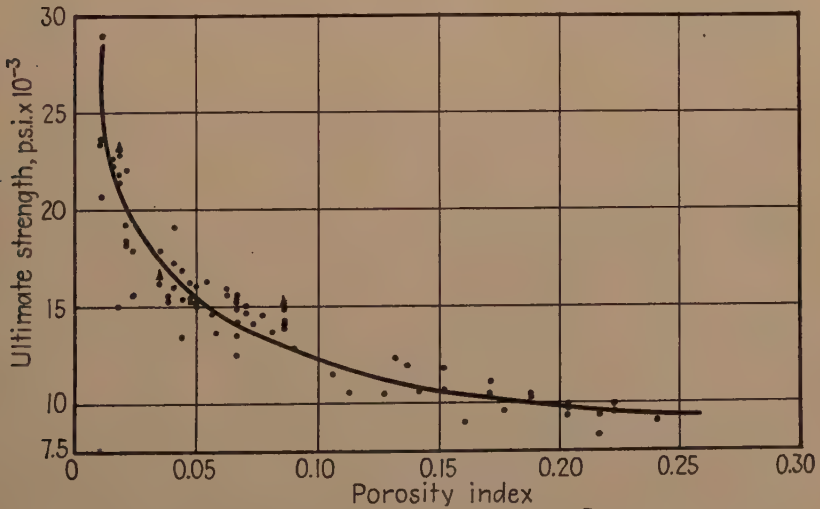


FIG. 7.—ULTIMATE STRENGTH VS. POROSITY INDEX, C ALLOY AS CAST.

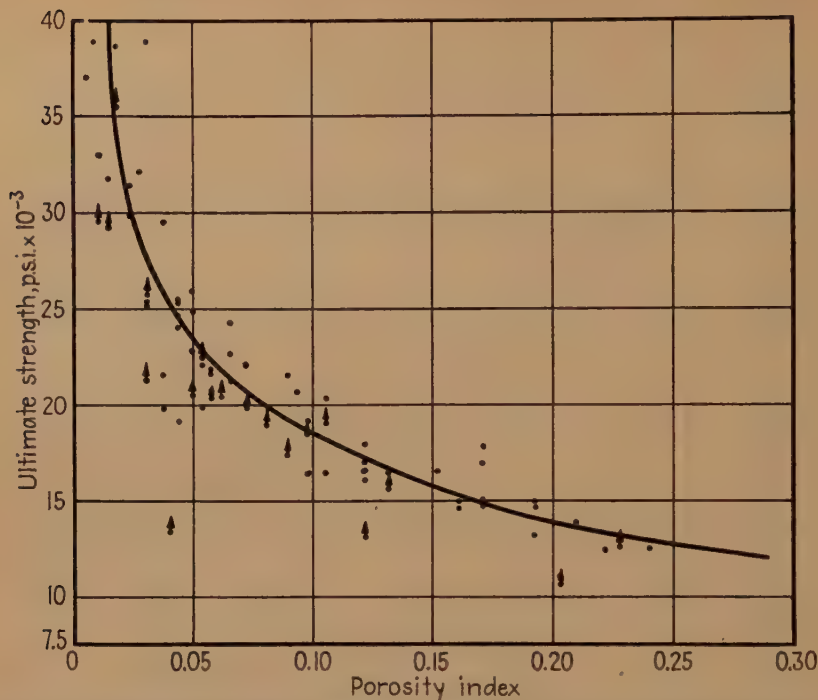


FIG. 8.—ULTIMATE STRENGTH VS. POROSITY INDEX, C ALLOY, SOLUTION-HEAT-TREATED.

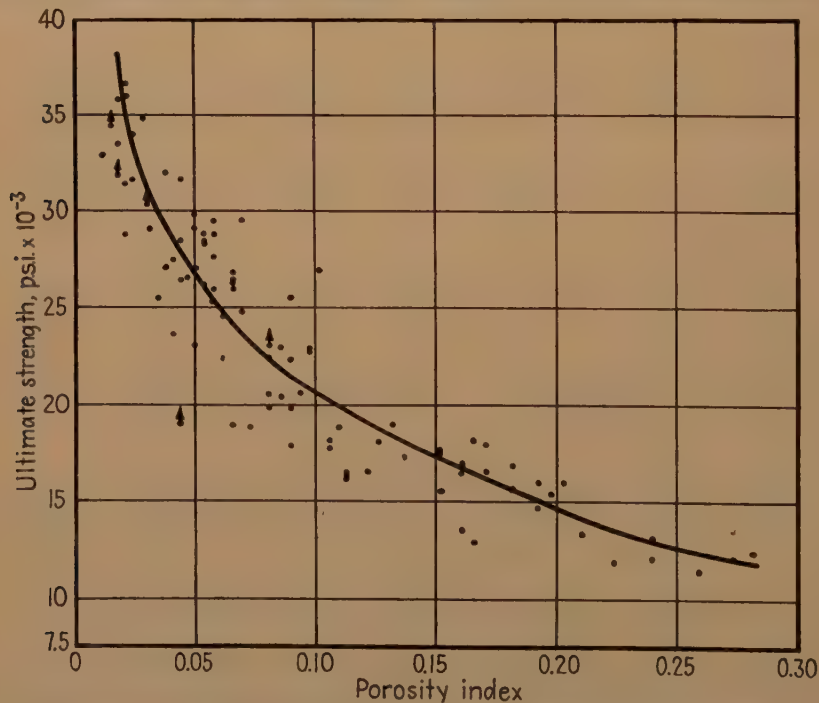


FIG. 9.—ULTIMATE STRENGTH VS. POROSITY INDEX, C ALLOY, SOLUTION-HEAT-TREATED AND AGED.

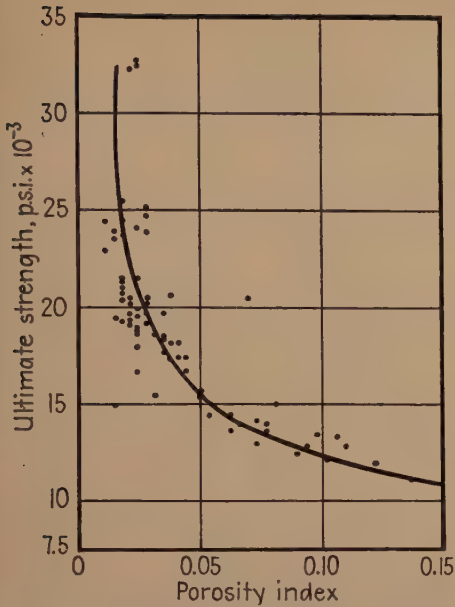


FIG. 10.—ULTIMATE STRENGTH VS. POROSITY INDEX, A8 ALLOY AS CAST.

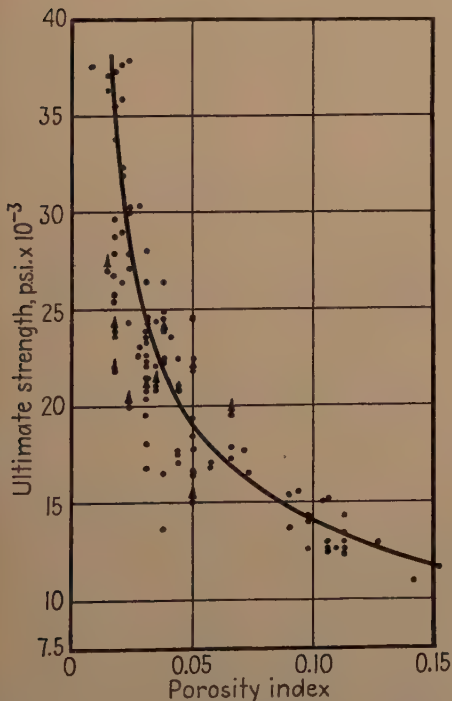


FIG. 11.—ULTIMATE STRENGTH VS. POROSITY INDEX, A8 ALLOY SOLUTION-HEAT-TREATED.

of the No. 1 test bars were averaged for each of the four alloys and two types of castings. The remainder of the bars, 2 through 8, were treated in the same

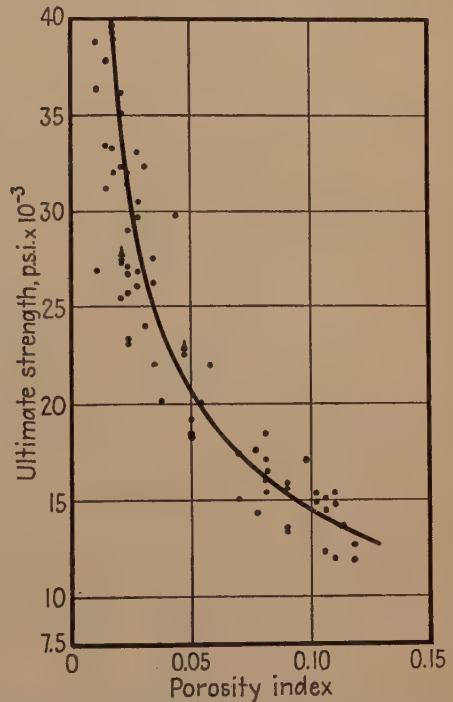


FIG. 12.—ULTIMATE STRENGTH VS. POROSITY INDEX, A8 ALLOY, SOLUTION-HEAT-TREATED AND AGED.

manner. Thus there were obtained two sets of eight average porosity indices for each alloy, representing the worst porosity conditions found in transversing each of two types of castings. These data are plotted as a function of the test-bar numbers, or location in the casting, to obtain the porosity survey curves shown in Figs. 28 and 29.

The number of castings and melts represented in the averages is shown in Table 2.

RESULTS

It is apparent from Figs. 28 and 29 that H alloy is considerably more susceptible

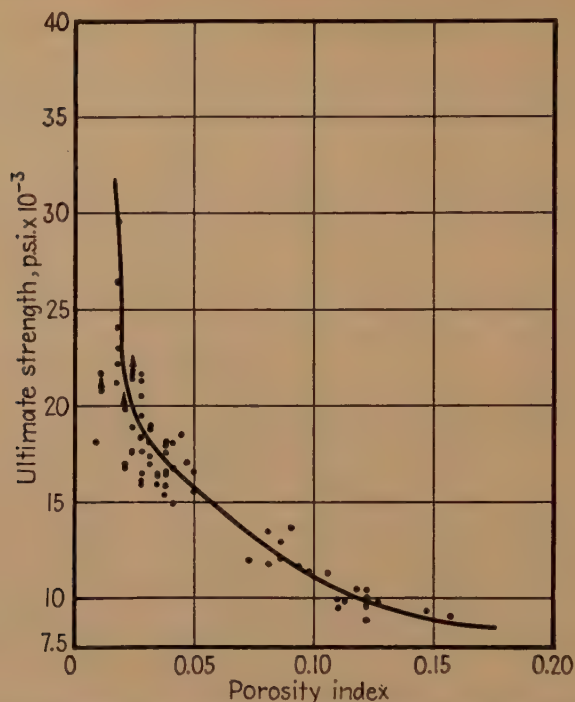


FIG. 13.—ULTIMATE STRENGTH VS. POROSITY INDEX, AZ91 ALLOY AS CAST.

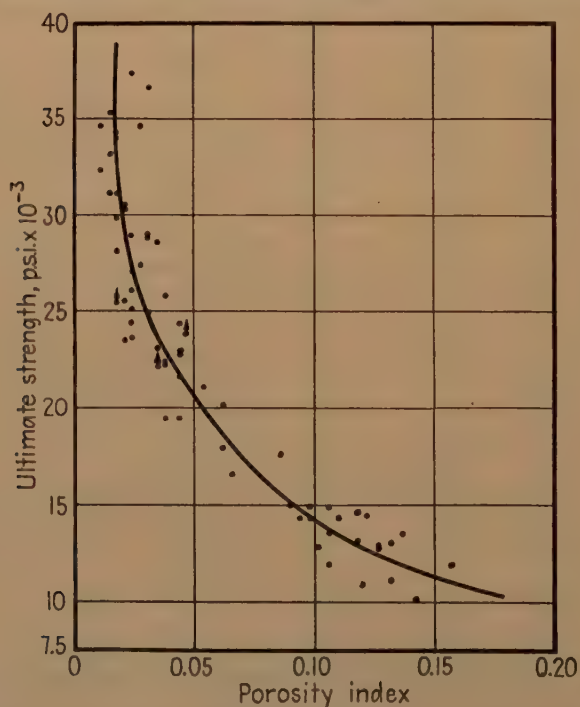


FIG. 14.—ULTIMATE STRENGTH VS. POROSITY INDEX, AZ91 ALLOY, SOLUTION-HEAT-TREATED.

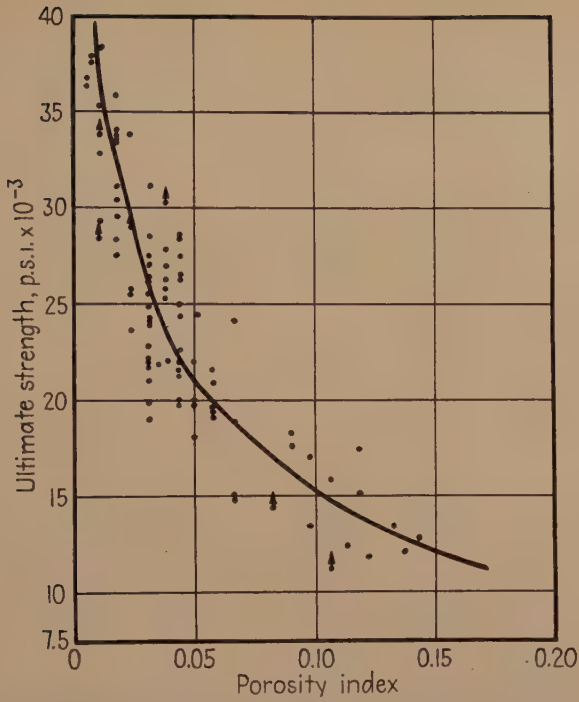


FIG. 15.—ULTIMATE STRENGTH VS. POROSITY INDEX, AZ91 ALLOY, SOLUTION-HEAT-TREATED AND AGED.

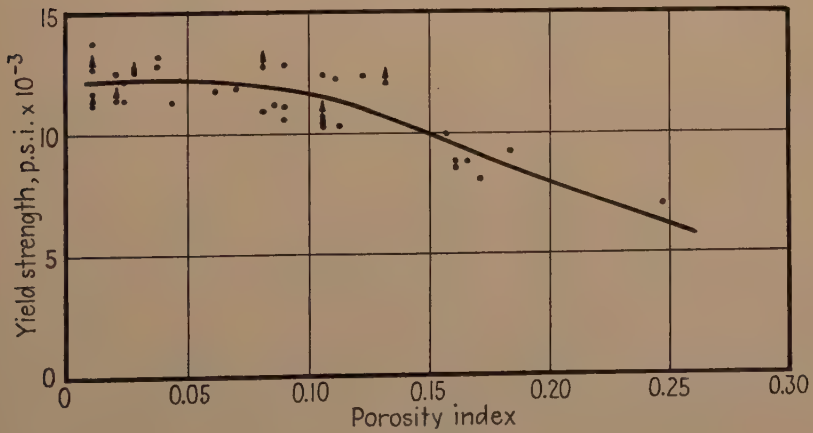


FIG. 16.—YIELD STRENGTH VS. POROSITY INDEX, H ALLOY AS CAST.

to microporosity than is C, and that A8 and AZ91 alloys are the least susceptible, being nearly equal in their response.

are believed to have relegated variations in dissolved gases between melts to a minor factor.

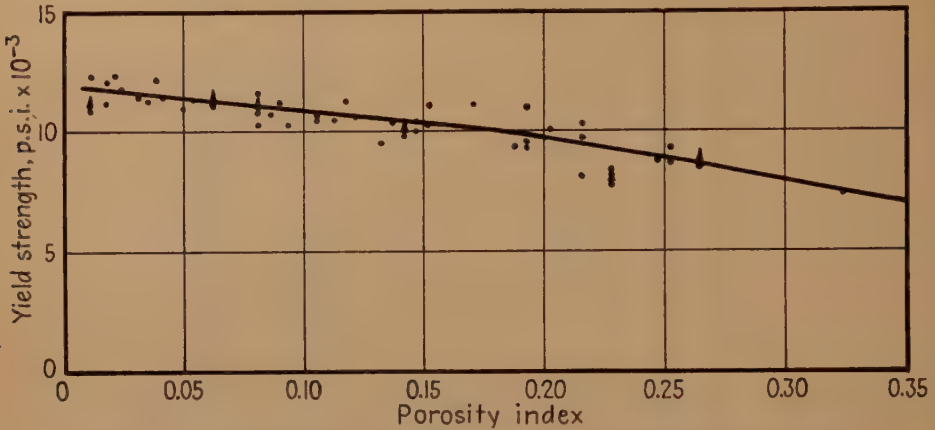


FIG. 17.—YIELD STRENGTH VS. POROSITY INDEX, H ALLOY, SOLUTION-HEAT-TREATED.

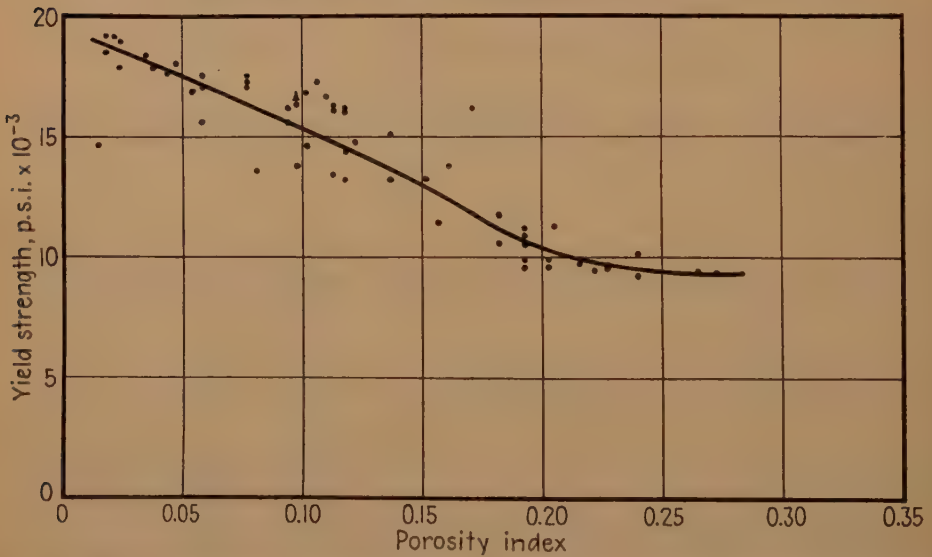


FIG. 18.—YIELD STRENGTH VS. POROSITY INDEX, H ALLOY SOLUTION-HEAT-TREATED AND AGED.

It is known that dissolved gases will aggravate microporosity in magnesium alloys, and consequently shift to some degree the measured relative susceptibility of the alloys to microporosity. Constant adherence to routine foundry procedure and use of flux from a sealed container

RADIOGRAPHIC CONTRAST OF FOUR ALLOYS

Small differences in zinc and aluminum contents of the four alloys exert an appreciable effect on the radiographic exposure time. For this reason it was desired to

determine what relative differences in radiographic contrast would be obtained when X-raying the different alloys. Increasing available contrast, of course,

CONCLUSIONS

The conclusions reached in this paper may be briefly stated:

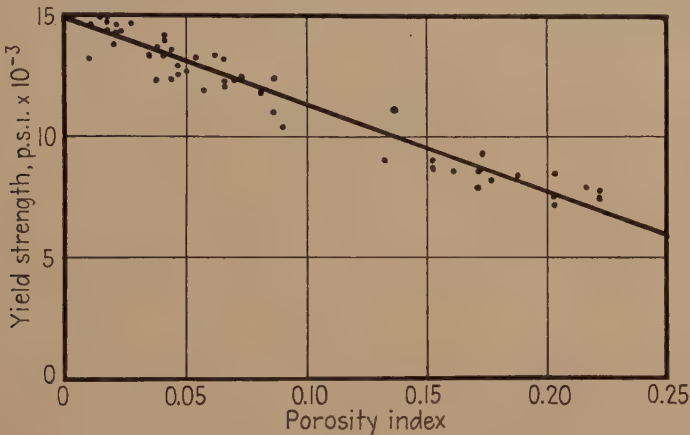


FIG. 19.—YIELD STRENGTH VS. POROSITY INDEX, C ALLOY AS CAST.

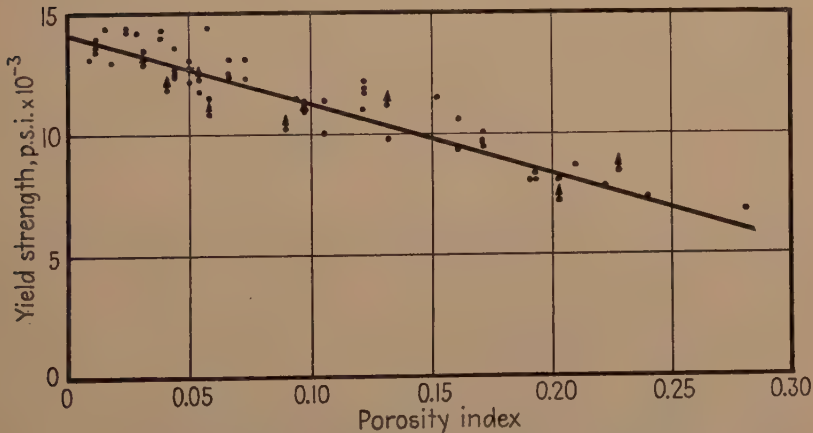


FIG. 20.—YIELD STRENGTH VS. POROSITY INDEX, C ALLOY, SOLUTION-HEAT-TREATED.

causes a given amount of porosity to appear increasingly severe in the radiograph. To supply data on this subject, identical step blocks of the four alloys were prepared and X-rayed with a procedure similar to that used for the test bars. The results are shown in Fig. 30. The differences in radiographic contrast for the four alloys is negligible as measured by the slopes of the graphs.

1. The order of increasing sensitivity of the four alloys to the deleterious effects of microporosity is as listed in Table 3.

The omission of the separating comma between any two of the alloys indicates that the alloys are similar in their response to the presence of microporosity.

2. Small quantities of microporosity cause a large decrease of ultimate tensile strength. The rate of decrease of ultimate

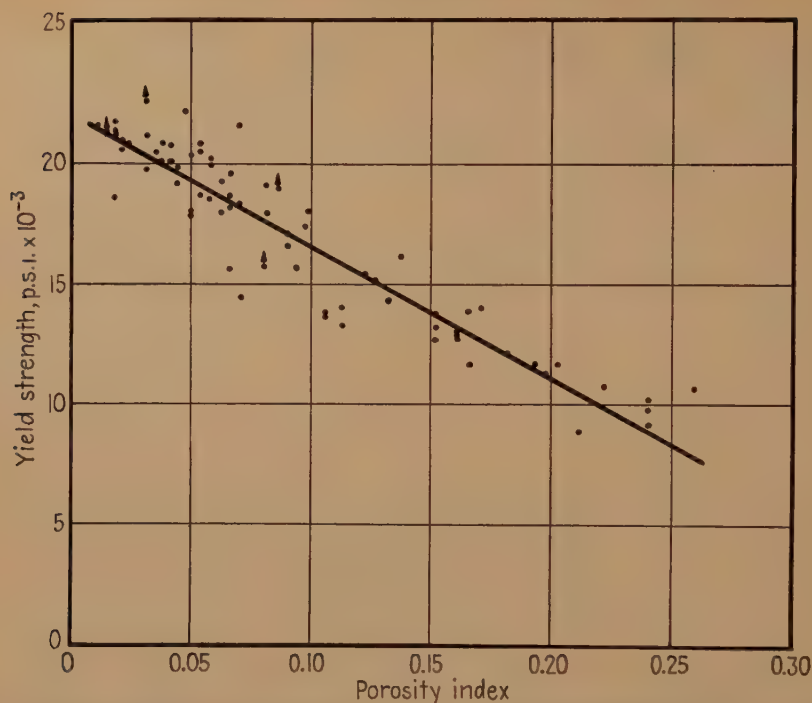


FIG. 21.—YIELD STRENGTH VS. POROSITY INDEX, C ALLOY, SOLUTION-HEAT-TREATED AND AGED.

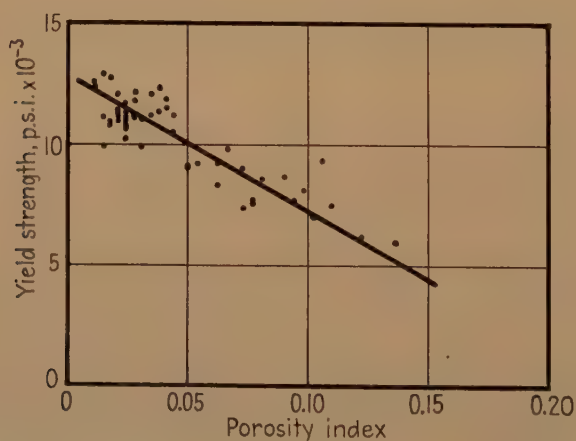


FIG. 22.—YIELD STRENGTH VS. POROSITY INDEX, A8 ALLOY AS CAST.

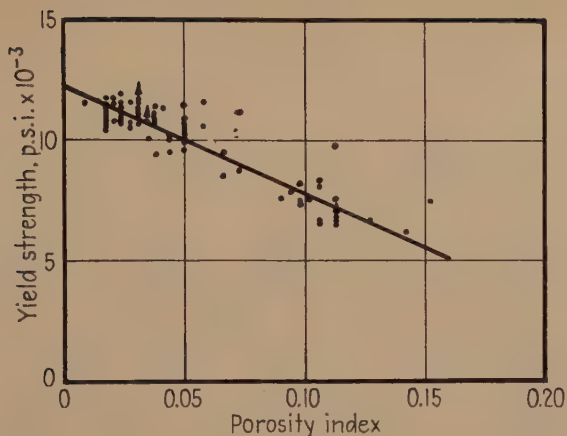


FIG. 23.—YIELD STRENGTH VS. POROSITY INDEX, A8 ALLOY, SOLUTION-HEAT-TREATED.

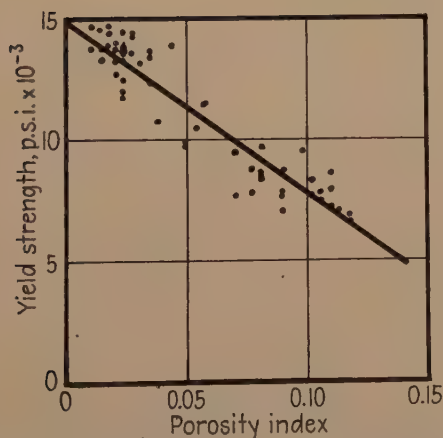


FIG. 24.—YIELD STRENGTH VS. POROSITY INDEX, A8 ALLOY, SOLUTION-HEAT-TREATED AND AGED.

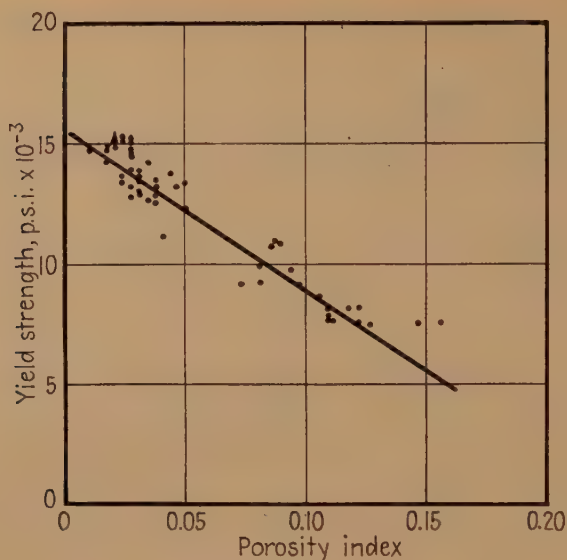


FIG. 25.—YIELD STRENGTH VS. POROSITY INDEX, AZ91 ALLOY AS CAST.

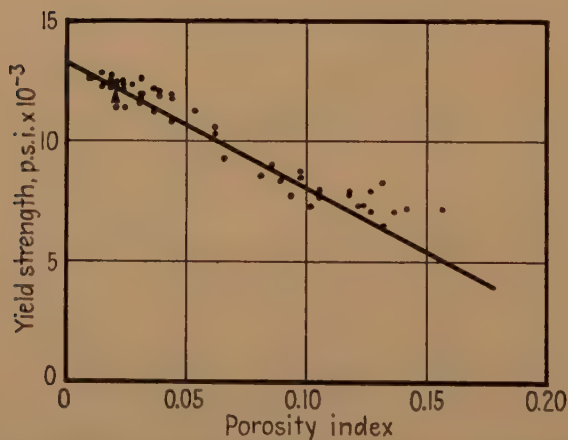


FIG. 26.—YIELD STRENGTH VS. POROSITY INDEX, AZ91 ALLOY SOLUTION-HEAT-TREATED

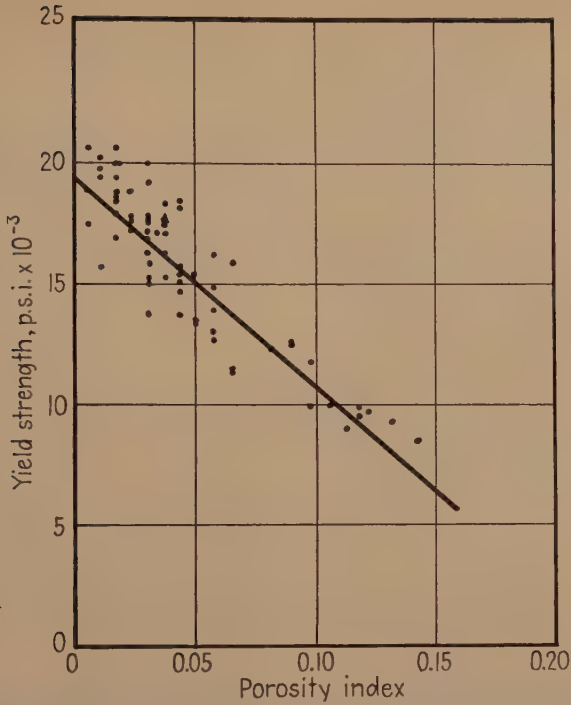


FIG. 27.—YIELD STRENGTH VS. POROSITY INDEX, AZ9 ALLOY, SOLUTION-HEAT-TREATED AND AGED.

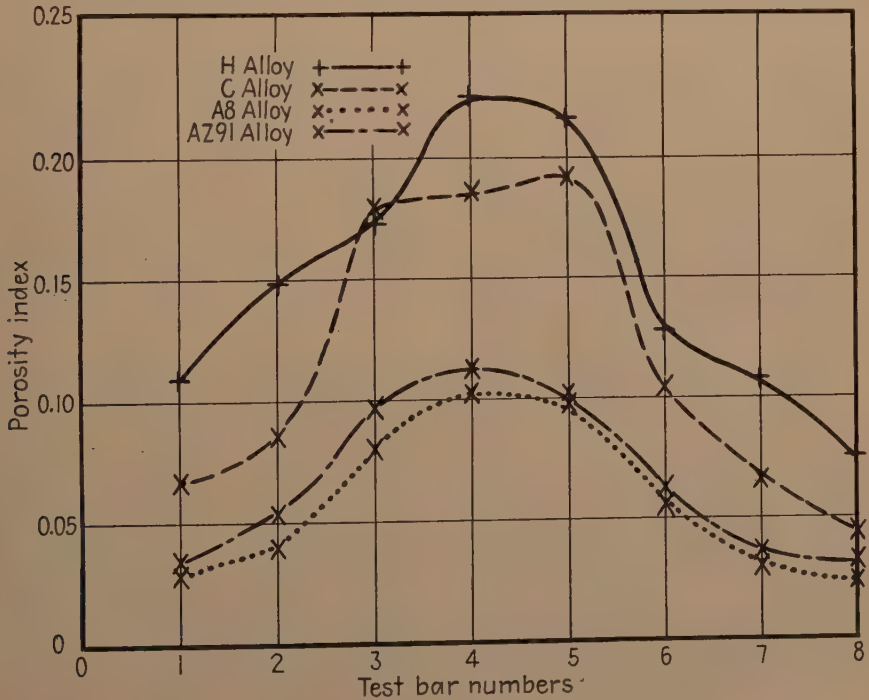


FIG. 28.—POROSITY SURVEY, HORIZONTAL PLATES, NO RISERS.

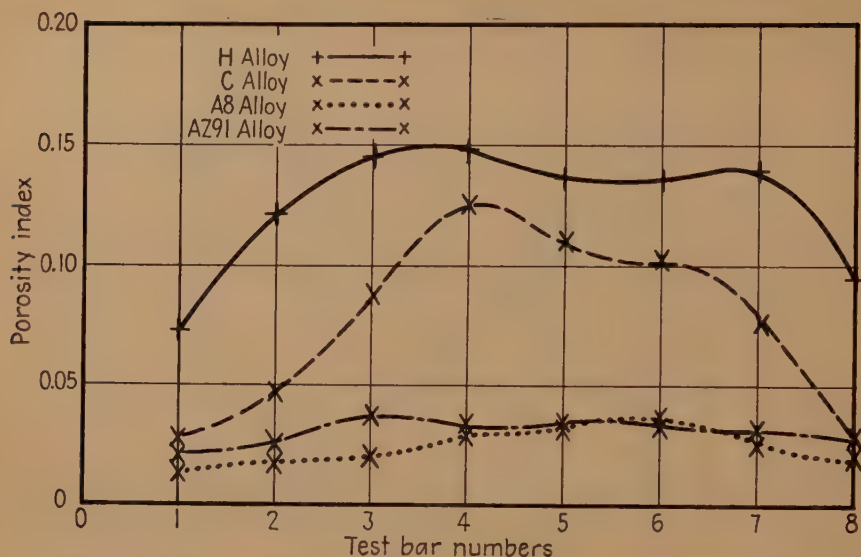


FIG. 29.—POROSITY SURVEY, HORIZONTAL PLATES, RISERS OVER CENTER.

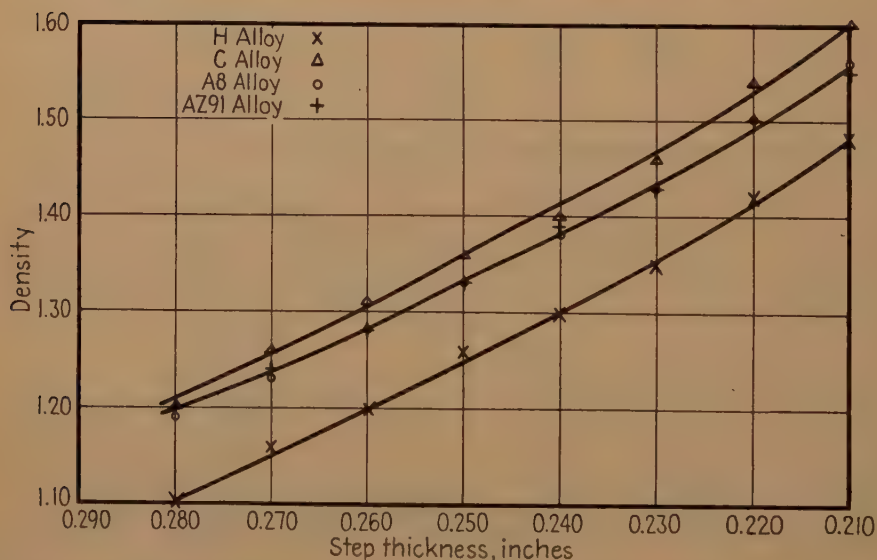


FIG. 30.—RADIOGRAPHIC CONTRAST OBTAINED ON STEP BLOCKS OF H, C, A8 AND AZ91 ALLOYS.

tensile strength becomes less as total microporosity becomes greater. Yield strength decreases linearly with increasing amounts of microporosity.

3. The order of increasing tendency of the four alloys to contain microporosity

when each is cast under identical conditions is A8, and AZ91, C, and H. Large differences exist in the tendency of H, C, and A8 alloys to contain microporosity. Only a small difference exists between A8 and AZ91.

TABLE 2.—Number of Castings and Melts Represented in Porosity Survey Curves

Alloy	Casting		Number of Heats ^a
	Type	Number Averaged	
H	Horizontal, no riser	13	2
C	Horizontal, no riser	22	3
A8	Horizontal, no riser	21	3
AZ91	Horizontal, no riser	19	4
H	Horizontal, riser over center	3	3
C	Horizontal, riser over center	3	3
A8	Horizontal, riser over center	3	3
AZ91	Horizontal, riser over center	3	3

^a Heats in second half of table are, in most cases, the same as those in first half.

- Dow Chemical Co. Report, Dec. 29, 1941.
2. C. Goddard: Notes on Magnesium Alloy Applications in Aircraft and Allied Industries and on Alloy Compositions. *Magnesium Review and Abstracts* (1944) 4, 2.
3. J. L. Walker: A Comparison of the Mechanical Properties of American and D. T. D. Type Bars in Various Magnesium Alloys. *Magnesium Review and Abstracts* (1942) 3, 1.
4. J. J. Casey: Foundry Procedures and Test Data of the Wright Field Magnesium Foundry. Eng. Div. Memorandum Rept. TSEAL-4-M4341 (July 1945).
5. L. Lasch: A Note on Sand-cast Plates for the Radiographic Assessment of Tendency to Microporosity in Magnesium Alloys. *Magnesium Review and Abstracts* (1942) 3, 2.
6. R. S. Busk: A Correlation of the Mechanical Properties and Radiographic Appearance of Magnesium Alloy Castings. Symposium on Radiography, Amer. Soc. Test. Mat. (1943).

TABLE 3.—Comparative Effect of Microporosity on Four Casting Alloys

Condition of Heat-treatment	Order, from Left to Right of Increasing Percentage Reduction of Ultimate Strengths By any Given Amount of Microporosity	Order, from Left to Right of Increasing Percentage Reduction of Yield Strength By any Given Amount of Microporosity
As-cast.....	H, C, A8 and AZ91	H, C, A8, AZ91
Solution-heat-treated..	H, C, A8 and AZ91	H, C, A8, AZ91
Solution-heat-treated and aged.....	H, C, A8 and AZ91	H, C, A8, AZ91

4. A negligible difference in radiographic contrast is obtained when X-raying H, C, A8 or AZ91 alloys.

ACKNOWLEDGMENT

Sincere appreciation is extended to Capt. P. W. Bakarian, of the Materials Laboratory, for his guidance and helpful criticism of this work. Thanks are due to Mr. Richard R. Kennedy, for his interest and permission to publish the paper.

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1. J. E. Dorn: The Application of Magnesium Alloys on the Junkers JU-88 Bomber.

DISCUSSION

(H. Y. Hunsicker presiding)

R. F. MARANDE.*—It is very interesting to note that Mr. Burns, using a different type of test casting, has found practically the same porosity tendency relationship between the various alloys he has investigated as we have.

H. Y. HUNSICKER.†—There is one point of considerable interest in this paper; that is, the attempt the author has made to distinguish between two factors that prevail in cast metals; (1) the susceptibility of the alloy to unsoundness, (2) the effect of a certain degree of unsoundness on the mechanical properties of the alloy, which might be termed its sensitivity to unsoundness. The author has shown examples of materials in which these two factors are to some extent compensating. I believe that this is a line of investigation that should be pursued more intensively.

J. D. HANAWALT.‡—This paper is one of several from various laboratories and the groundwork has been pretty well laid for a comparison of the alloys with which it deals.

* The Dow Chemical Co., Midland Michigan.

† Aluminum Company of America, Cleveland, Ohio.

‡ Director of Metallurgical Department, The Dow Chemical Co., Midland, Michigan.

Some Properties of Sand-cast Alloys in the Magnesium-rich Corner of the Magnesium-aluminum-zinc System

BY R. S. BUSK* AND R. F. MARANDE*

(Chicago Meeting, February 1946)

THE magnesium-aluminum-zinc system contains most of the magnesium-base alloys used commercially, although in practice the ternary alloys are usually modified by the addition of a small amount providing reference material, and to aid in the choice of a commercial alloy to serve a particular purpose. Detailed, critical analysis of the commercial alloys has been covered in a previous paper.¹

TABLE I.—Some Typical Commercial Magnesium Alloys

Alloy			Country	Composition, Per Cent			Tensile Properties								
							As-cast			Heat-treated			Aged		
							% E		1000 Lb. per Sq. In.	% E		1000 Lb. per Sq. In.	% E		1000 Lb. per Sq. In.
A.S.-T.M.	Dow	Foreign		Al	Zn	Mn		Y.S.	T.S.		Y.S.	T.S.		Y.S.	T.S.
A8	A		U. S.	8	0	0.13	5	12	30	13	11	39	7	16	39
A10	G		U. S.	10	0	0.10	1	16	24	10	14	39	2	20	39
AZ63	H		U. S.	6	3	0.15	6	14	30	12	14	40	5	19	40
AZ92	C		U. S.	9	2	0.10	2	14	24	10	16	40	2	23	40
		AZ31 ^a	Germany	3	1	0.3	8.5		23.8						
		AZ6 ^a	Germany	4	3	0.3	7.5		25.1						
		Ag ^a	England	8.5	0.5	0.15				10		38	4.5		38
		A10 ^a	Ger.-Eng.	9.5	0.5	0.10				9		38	3		38

* Taken from Beck.¹

of manganese. Table 1 contains the magnesium-base commercial sand-casting alloys most widely used throughout the world, together with their typical tensile properties.

These alloys may be regarded as a single family of varying aluminum and zinc content, disregarding manganese. A concise means of presenting data for them is by means of iso-property lines plotted on triangular coordinate paper.

Constitutional, casting, and mechanical properties are presented in this manner. The data are given with the object of

All alloys reported were made in 15-lb. melts, superheated to 1700°F. for 15 min., cooled to 1400°F. and poured in sand molds. The test bars produced had a 1/2-in. reduced section and were about 6 in. long. Except for the data represented in Figs. 1 and 3 the alloys used were of commercial purity and contained 0.1 to 0.2 per cent Mn in addition to the aluminum and zinc.

CONSTITUTIONAL DATA

Under the heading of Constitutional Data are included all known data on con-

Manuscript received at the office of the Institute Dec. 1, 1945. Issued as T.P. 2009 in METALS TECHNOLOGY, June 1946.

* The Dow Chemical Company, Midland, Michigan.

¹ References are at the end of the paper.

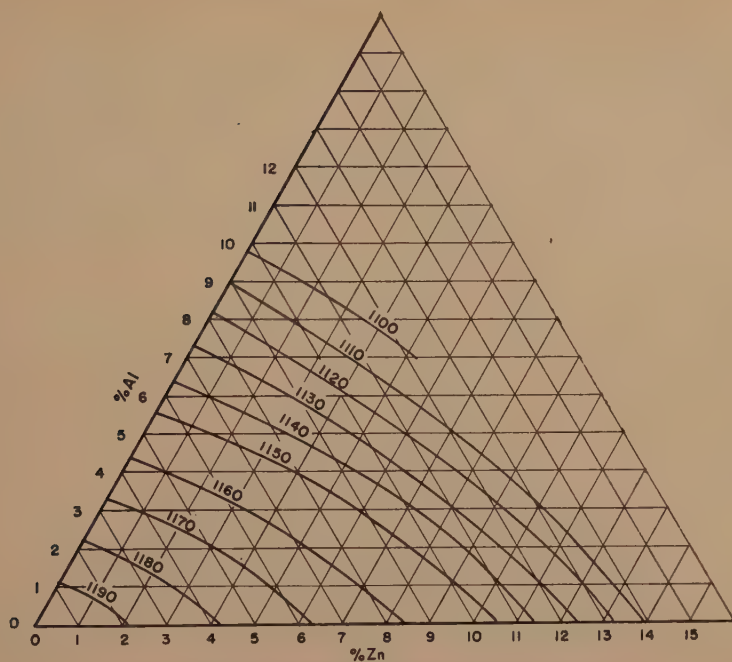


FIG. 1.—LIQUIDUS TEMPERATURES, DEGREES FAHRENHEIT.

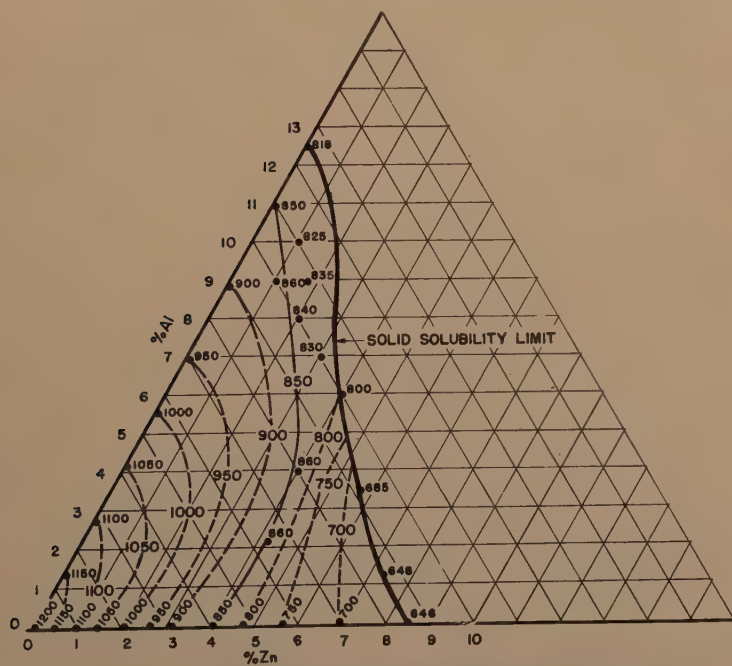


FIG. 2.—SOLIDUS TEMPERATURES, DEGREES FAHRENHEIT.

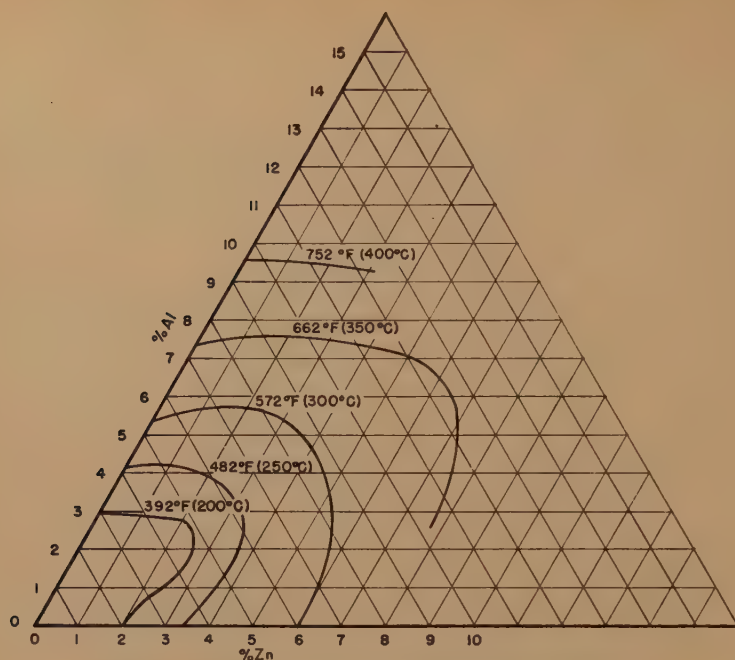


FIG. 3.—SOLVUS TEMPERATURES, DEGREES FAHRENHEIT.

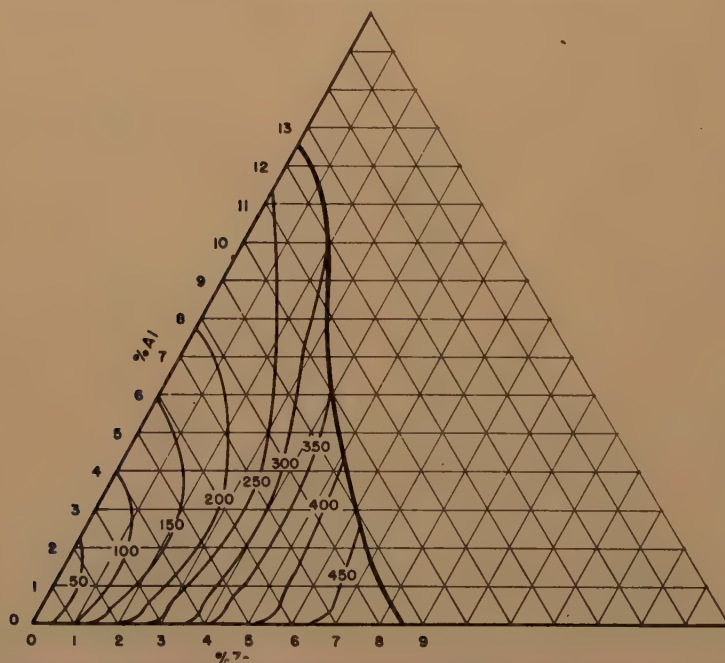


FIG. 4.—ESTIMATED EQUILIBRIUM FREEZING RANGE, DEGREES FAHRENHEIT. TEMPERATURE DIFFERENCE BETWEEN LIQUIDUS AND SOLIDUS.

stitutional diagrams, under both equilibrium and nonequilibrium conditions.

Equilibrium Conditions

The data for the liquidus temperatures of the Mg-Al-Zn systems are plotted in Fig. 1.² These curves will show the true

data represent the temperatures of final freezing under equilibrium conditions. Since these depend upon complete diffusion in the solid state, and this rarely takes place, true freezing conditions during normal casting are not represented by the solidus surface.

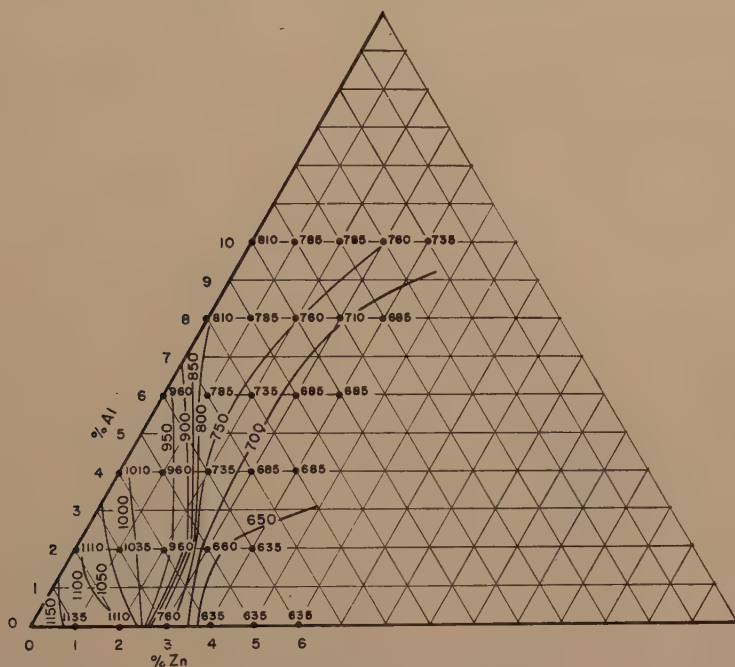


FIG. 5.—NONEQUILIBRIUM SOLIDUS, DEGREES FAHRENHEIT. SOLIDUS SURFACE RESULTING FROM COOLING RATE OBTAINED IN SAND MOLD.

condition as long as the liquid composition is uniform prior to freezing and there is no undercooling. Since the former condition usually prevails and undercooling is limited to about 2°F.,³ Fig. 1 remains true during normal casting.

In Fig. 2 are given the solidus temperatures for the same composition range. The data for this surface were taken from work in the binary systems Mg-Al and Mg-Zn,² together with some limited and preliminary data within the ternary section obtained in the Dow laboratories. The surface represented in Fig. 2 must be considered as an approximation only. The

The equitemperature lines for the solidus are plotted in Fig. 3.² More recent data obtained in the laboratory of the Dow Chemical Co. indicate that the maximum solid solubility may not be as great as shown by the 662°F. isotherm (Fig. 2). This represents the temperature of the solid-solubility surface for the various compositions. Even though the data are for equilibrium conditions, this surface has practical use in precipitation and homogenization heat-treatments.

The difference in temperature between the curves of Figs. 1 and 2 at a given composition is plotted in Fig. 4 to give the

equilibrium freezing range. This range is narrower than that actually met with in practice because the solidus is always depressed in nonequilibrium cooling.

genization of the specimen during the heating and holding period; however, metallographic examination of one composition confirmed that incipient brittleness and

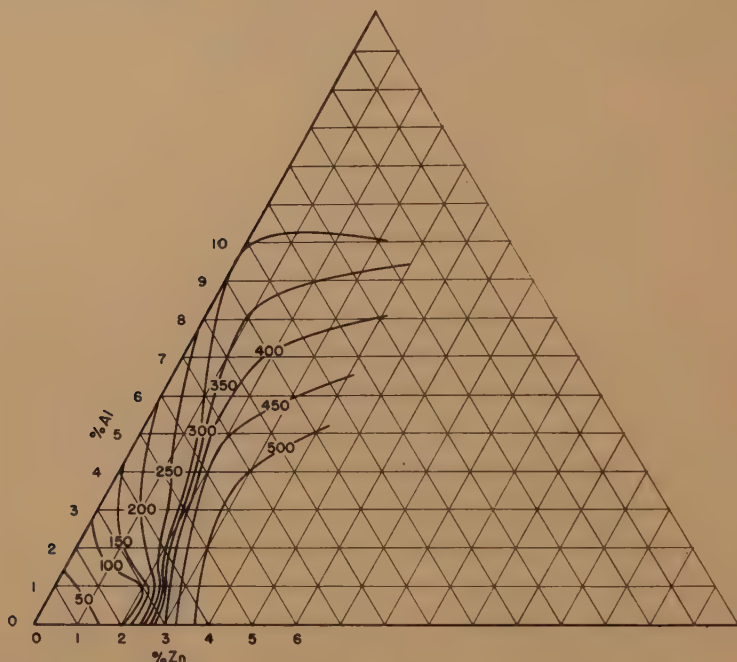


FIG. 6.—NONEQUILIBRIUM FREEZING RANGE, DEGREES FAHRENHEIT. TEMPERATURE DIFFERENCE BETWEEN LIQUIDUS AND NONEQUILIBRIUM SOLIDUS.

Nonequilibrium Conditions

Fig. 5 shows the pseudo-solidus surface, representing the temperature at which the last metal solidifies in normal sand-casting practice. These data were obtained by pulling as-cast test bars at various temperatures, to determine the temperature at which each broke with a brittle fracture. The grips of the tensile-testing machine were put on a test bar and the bar was inserted in a salt bath. A thermocouple on the test bar enabled determination of the time to reach the desired temperature. After a 10-min. waiting period at temperature, the bar was pulled. This method led to results slightly higher than the true solidus of the piece, owing to some homo-

fusion occur at the same temperature within 5°F. Fig. 5 should be compared with Fig. 2, to determine the degree the solidus is depressed by nonequilibrium cooling.

The freezing range in normal sand-casting practice is shown in Fig. 6, obtained by taking the difference in temperature at a given composition between Fig. 1 and Fig. 2.

Considerable importance has been attached to the freezing range of casting alloys. Undoubtedly it has an effect on the fluidity and the ability to feed. However, the relative amounts of liquid and solid present at a given distance through the freezing range is at least as important as the length of the range.

CASTING AND HEAT-TREATMENT PROPERTIES

Foundry

The porosity tendency of the magnesium-rich alloys in the Mg-Al-Zn system was

tendency to be porous than either H or C. The low point in the region of Mg + 8 per cent Al + 3 per cent Zn, however, was not completely verified when used in commercial castings. This composition is also difficult to heat-treat, and, con-

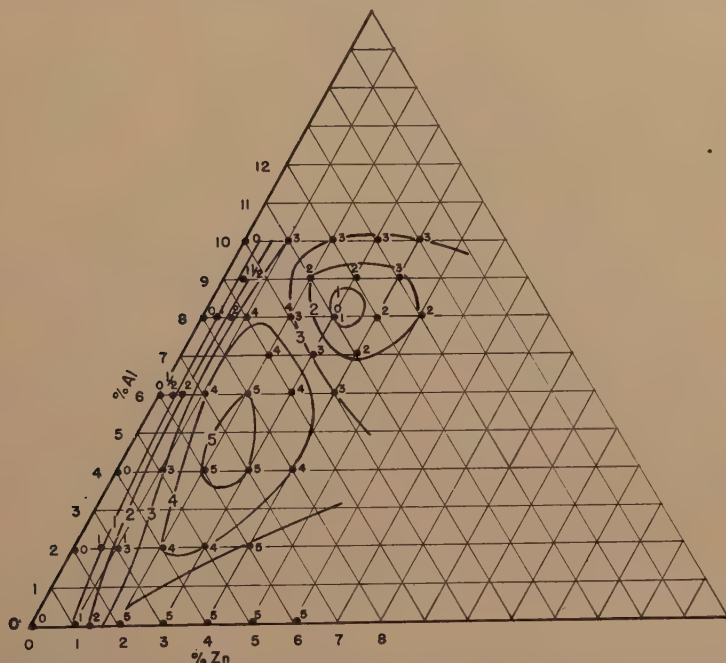


FIG. 7.—POROSITY TENDENCY. RELATIVE AMOUNT OF POROSITY OBTAINED IN PANELS CAST UNDER CONTROLLED CONDITIONS.
o = low porosity; 5 = high porosity.

determined by means of the rectangular panel described in a previous paper.¹ Two panels were poured for each alloy composition and were radiographed. The porosity in each set was then rated from zero to 5, according to an arbitrary scale in which zero designates no radiographic porosity while 5 means that the panel is porous throughout its entire length. The data are plotted in Fig. 7.

These data have been found to correlate fairly well with foundry experience on various alloys. For example, C alloy is less porous in the commercial foundry than H alloy, while A alloy shows a lower

sequently, has not been developed as a commercial alloy.

Fig. 7 indicates that the low-zinc alloys are quite sound and that the maximum porosity tendency is in the region of 4 to 6 per cent Al and 1.5 to 3 per cent Zn. The porosity tendency rises very rapidly as small amounts of zinc are added to the Mg-Al binary alloys.

The solid shrinkage of sand-cast Mg-Al-Zn alloys is shown in Fig. 8. The data were obtained by casting a tapered bar 48 in. long. The cross section of the bar was approximately $1\frac{1}{4}$ by $\frac{7}{8}$ in. at the large end, tapering down to $\frac{3}{4}$ by $\frac{5}{8}$ in.



FIG. 8.—SHRINKAGE, 0.01 INCHES. FREE CONTRACTION IN SAND MOLD OF BAR 48-INCHES LONG.

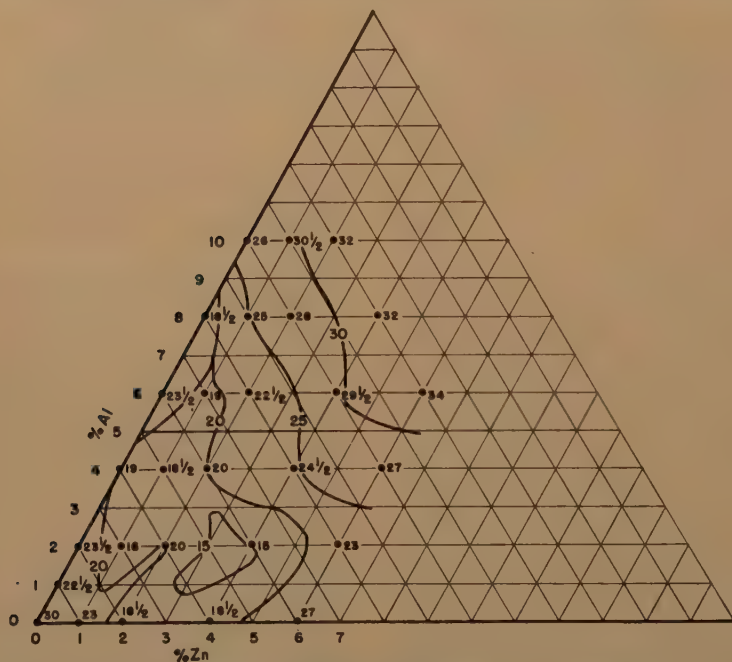


FIG. 9.—FLUIDITY, INCHES. LENGTH OF SPIRAL AS OBTAINED IN CONVENTIONAL SPIRAL TYPE OF FLUIDITY MOLD.

All alloys poured at 1400°F.

at the small end. The gate was at the large end of the bar, which was rigidly anchored to the flask by casting around steel screw stock. The small end was free to move,

sarily include the liquid shrinkage of the metal. They do have value, however, in deciding the relative merits of the Mg-Al-Zn alloys where shrinkage is important.

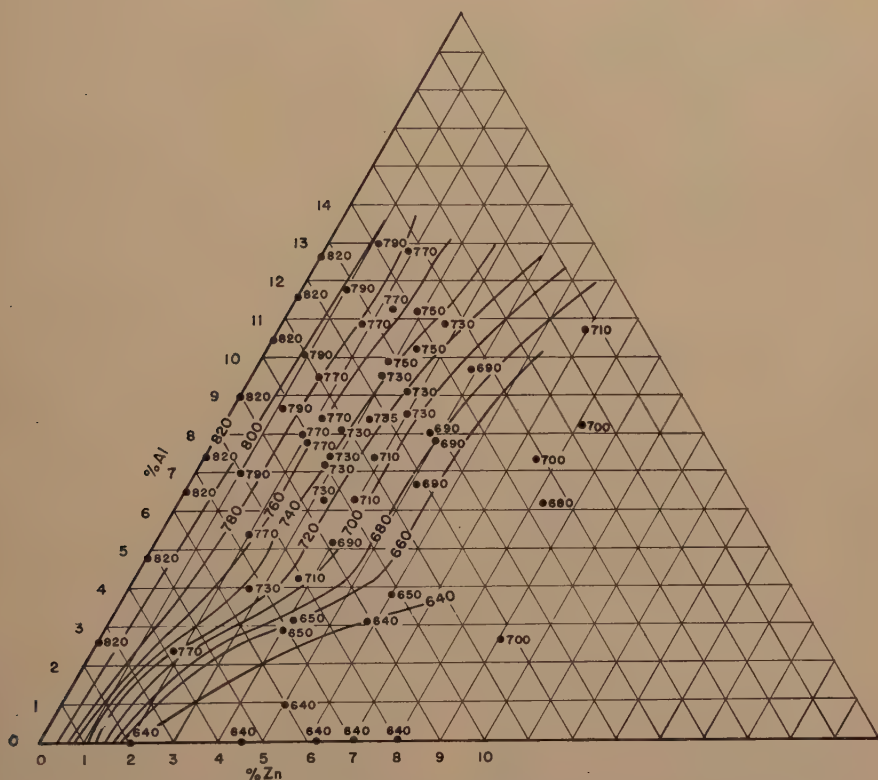


FIG. 10.—HEAT-TREATMENT TEMPERATURES, DEGREES FAHRENHEIT. MAXIMUM PRACTICAL TEMPERATURES ASSUMING TWO-HOUR PREHEAT FROM 640°F. TO TEMPERATURE.

but was also cast around steel screw stock. As the cast bar contracted after pouring, the free end would move and the shrinkage could be read in hundredths of an inch on a steel scale located outside the flask. The data of Fig. 8 represent the difference in length of the 48-in. bar immediately after casting and its length at room temperature expressed in hundredths of an inch. The shrinkage gradually decreases with the addition of both aluminum and zinc. These figures cannot be used in pattern design because they do not neces-

sarily include the liquid shrinkage of the metal. They do have value, however, in deciding the relative merits of the Mg-Al-Zn alloys where shrinkage is important.

The fluidity data of the Mg-Al-Zn alloys are plotted in Fig. 9. The data were obtained by pouring the various alloys, at a temperature of 1400°F., into a conventional spiral-type fluidity mold.⁶ The numbers represent the length of the spiral in inches. In general, the alloys containing between 1 and 2 per cent Al and 3 to

4 per cent Zn show a minimum fluidity. Beyond this area the fluidity increases with increasing aluminum and zinc content.

Heat-treatment

Magnesium-alloy castings are generally given a solution heat-treatment to increase strength and ductility. It is desirable to heat-treat at as high a temperature as possible, to facilitate solution of the second-phase material. The maximum temperature, however, is limited by at least two practical considerations: the tendency of certain constituents in the alloys to melt and produce voids;⁶ and the increased tendency for complex shapes to sag as the temperature is raised. Surface oxidation is not a factor, because of the use of a 1.0 per cent SO_2 atmosphere.

The heat-treating temperature is chosen just below the point where neither melting of the second phase (burning) nor excessive sagging will occur. The temperature at which melting of the second phase takes place for a given nominal composition is influenced by the degree of segregation. Therefore, it is necessary to preheat below the final heat-treating temperature to partly homogenize the metal and thus raise the temperature at which melting will occur. Incipient fusion will occur at some temperature between the equilibrium solidus as given by Fig. 2 and the nonequilibrium solidus as given in Fig. 5. The exact point depends upon the amount of preheat that can be given economically. Usually this is considered to be about 2 hr., extending over the range of 500°F. to the final heat-treating temperature. This period of time was selected in obtaining the data for Fig. 10.

The other limiting factor, sagging, was determined by loading a test bar as a cantilever beam and noting the amount of permanent set that occurred after 15 hr. at temperature. Production experience has shown that the sagging of C alloy at 770°F. is about the maximum

that can be conveniently tolerated. Therefore, the permanent set obtained in the cantilever test with C alloy at 770°F. was taken as the limiting figure.

The maximum heat-treating temperatures, considering the two limiting factors of incipient fusion and sagging, are given in Fig. 10. It is evident that zinc lowers the maximum heat-treating temperature, while additions of aluminum raise it.

Comparing Fig. 10 with Fig. 5, it will be found that the maximum heat-treating temperatures in the central portion of the figure tend to be slightly higher than the nonequilibrium solidus. On the other hand, the heat-treating temperatures in both the low aluminum and the high-aluminum regions of Fig. 10 are below the incipient fusion point as given in Fig. 5. This may be explained by the fact that sagging is the limiting factor for the heat-treating temperature of the alloys containing small amounts of aluminum, while with high amounts of aluminum (plus zinc) the preheat does not appreciably lower the incipient fusion temperature.

The subject of germination or excessive grain growth during heat-treatment is completely covered in a previous publication.⁷ It is shown there that germination, as determined by the test used, is restricted to a limited region, defined roughly by the triangle Mg + 8.5 per cent Al, Mg + 13 per cent Al, and Mg + 8.5 per cent Al + 3 per cent Zn. Even within this region germination can be avoided by proper use of gates, risers, and chills, and by use of a special heat-treatment.⁷

MECHANICAL PROPERTIES

Room-temperature tensile properties were obtained on bars in the as-cast; heat-treated; heat-treated, air-cooled and aged; and heat-treated, quenched and aged conditions. In addition, the properties at 300°F. were measured for bars in the heat-treated, air-cooled and aged condition. Testing was done on unmachined con-

ventional test bars cast to size. The properties of four bars were averaged for each point. Heat-treatments were at the temperatures specified in Fig. 10 for a suf-

strength in the solution-heat-treated alloys is obtained in the upper portion of Fig. 16.

Comparison of the as-cast with the heat-treated properties shows no improvement

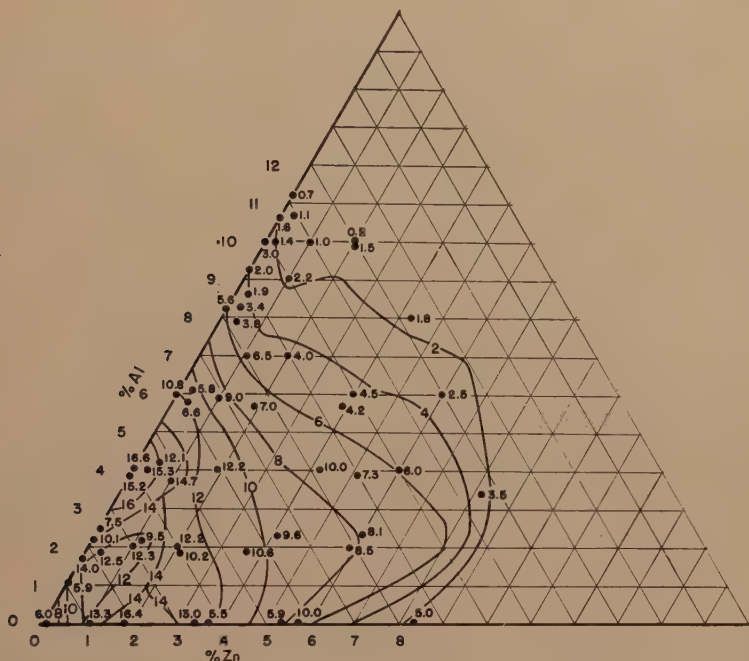


FIG. 11.—PERCENTAGE ELONGATION IN 2 INCHES AT ROOM TEMPERATURE. AS CAST.

ficient number of hours in each case to effect good solution. Aging was uniformly for 15 hr. at 350°F.

Room Temperature

All the data in the as-cast, solution-heat-treated, and solution-heat-treated and aged conditions are given in Figs. 11 to 19, inclusive. In the as-cast state both the elongation and tensile strength have a maximum at about 4 to 6 per cent Al and 0 to 1 per cent Zn. The yield strength in the as-cast state increases uniformly with the addition of aluminum and zinc.

In the solution-heat-treated state the maximum for percentage of elongation has been spread to include 4 to 9 per cent Al and 0 to 2 per cent Zn. Maximum tensile

after heat-treatment in alloys with less than 4 per cent total alloy content. Heat-treatment does not appreciably change the yield strength.

Aging after solution heat-treatment has little effect on alloys below a total alloy content of about 5 per cent except for the binary zinc alloys, in which a definite effect is noticed at about 4 per cent Zn. The elongation is lowered and the yield strength is raised considerably by aging after solution heat-treatment. There is a slight tendency for the tensile strength to be higher after aging than before.

The yield and tensile-strength data on alloys heat-treated, quenched,⁸ and aged are given in Figs. 20 and 21, respectively. The maximum yield is obtained around 12

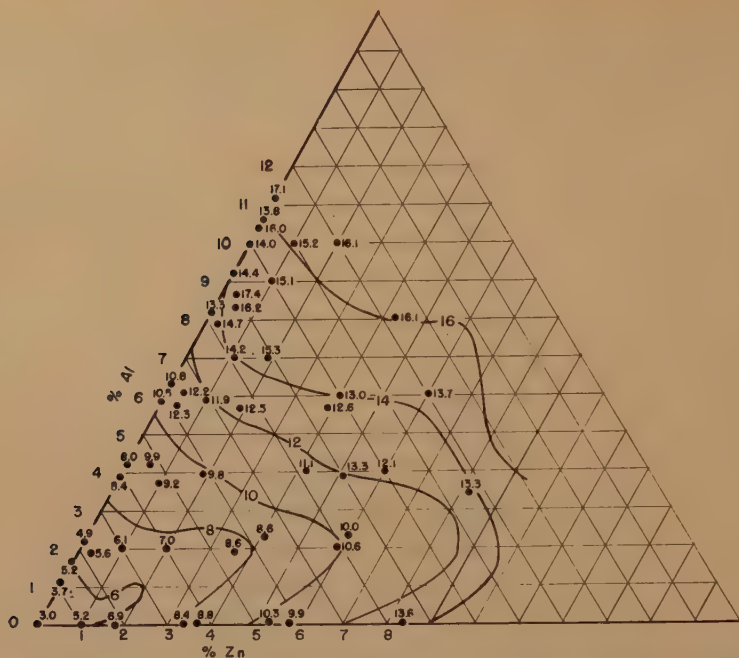


FIG. 12.—YIELD STRENGTH AT ROOM TEMPERATURE, 1000 POUNDS PER SQUARE INCH. AS CAST.

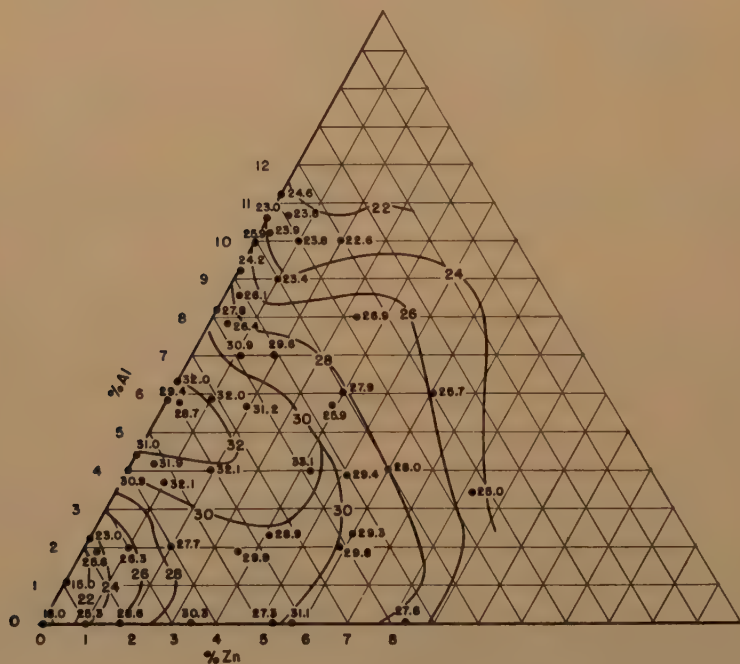


FIG. 13.—TENSILE STRENGTH AT ROOM TEMPERATURE, 1000 POUNDS PER SQUARE INCH. AS CAST.



FIG. 14.—PERCENTAGE ELONGATION IN 2 INCHES AT ROOM TEMPERATURE. HEAT-TREATED.

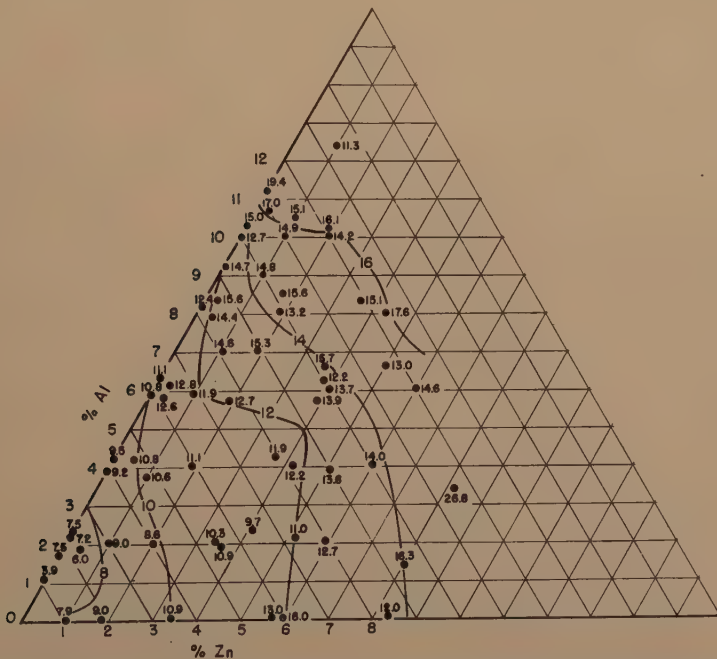


FIG. 15.—YIELD STRENGTH AT ROOM TEMPERATURE, 1000 POUNDS PER SQUARE INCH. HEAT-TREATED.



FIG. 16.—TENSILE STRENGTH AT ROOM TEMPERATURE, 1000 POUNDS PER SQUARE INCH. HEAT-TREATED.

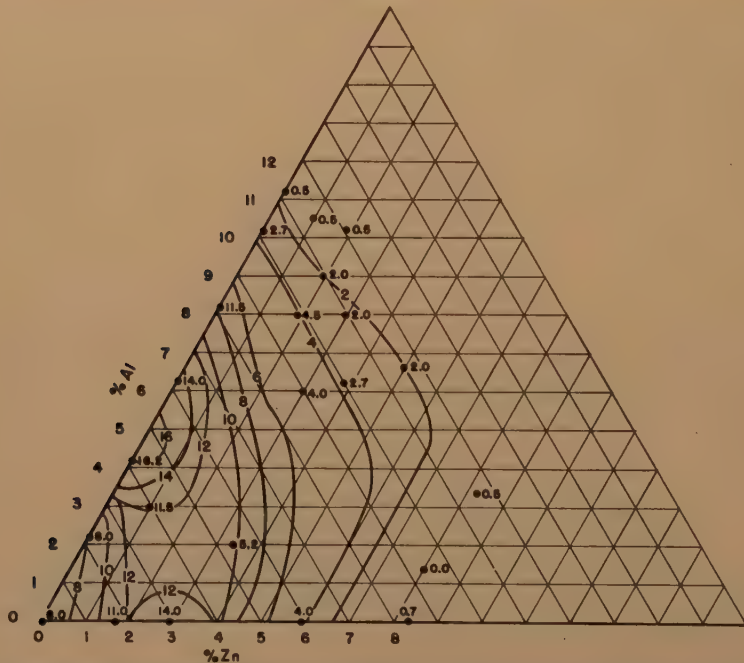


FIG. 17.—PERCENTAGE ELONGATION IN 2 INCHES AT ROOM TEMPERATURE. HEAT-TREATED AND AGED.

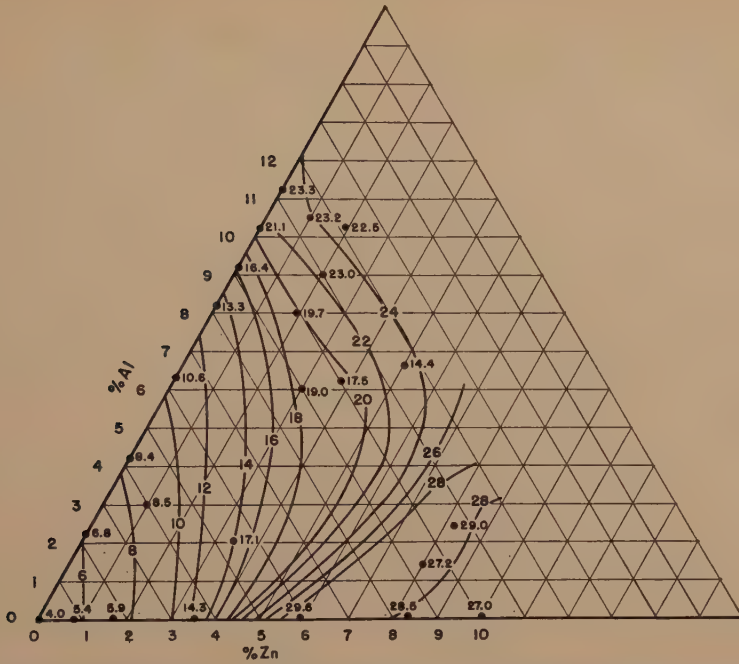


FIG. 18.—YIELD STRENGTH AT ROOM TEMPERATURE, 1000 POUNDS PER SQUARE INCH. HEAT-TREATED AND AGED.

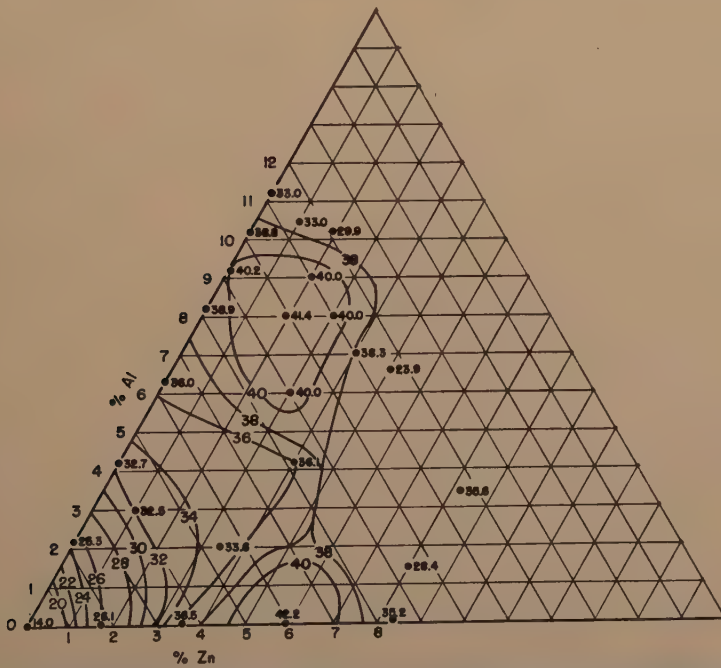


FIG. 19.—TENSILE STRENGTH AT ROOM TEMPERATURE, 1000 POUNDS PER SQUARE INCH. HEAT-TREATED AND AGED.

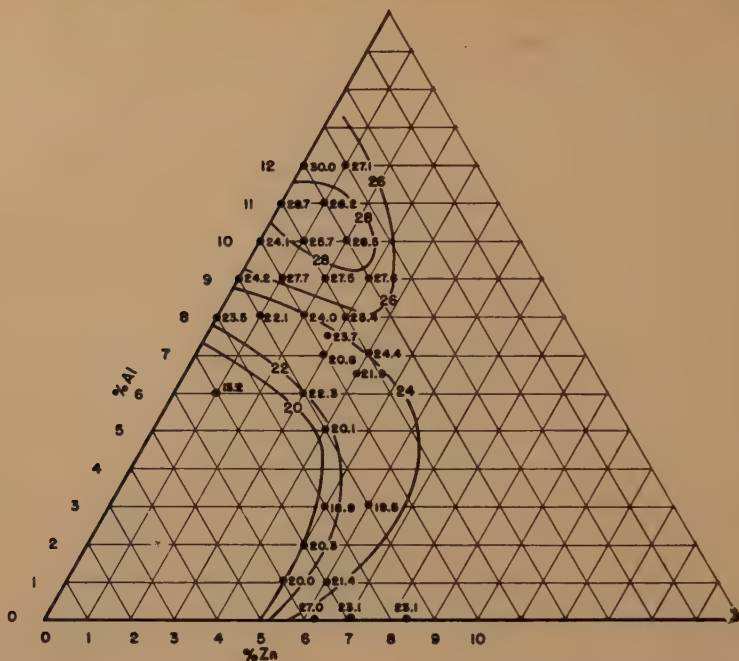


FIG. 20.—YIELD STRENGTH AT ROOM TEMPERATURE, 1000 POUNDS PER SQUARE INCH. HEAT-TREATED, QUENCHED AND AGED.

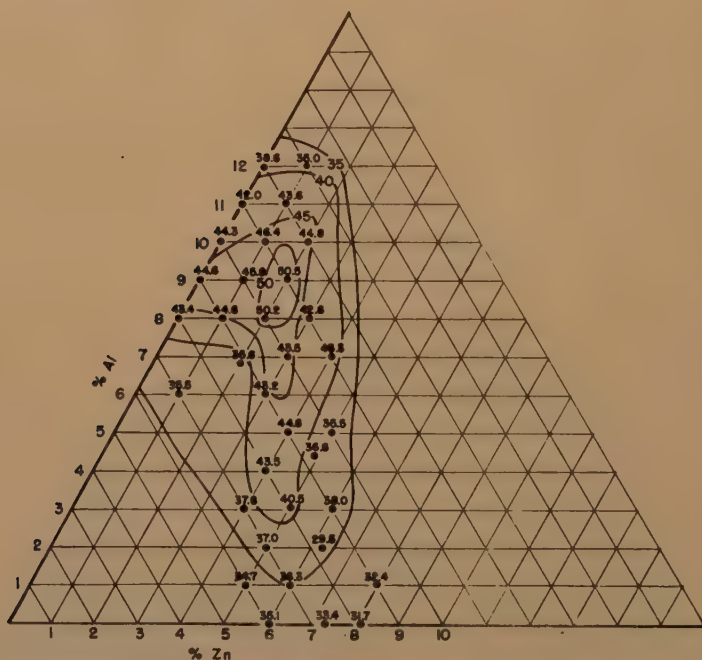


FIG. 21.—TENSILE STRENGTH AT ROOM TEMPERATURE, 1000 POUNDS PER SQUARE INCH. HEAT-TREATED, QUENCHED AND AGED.

per cent Al and 0 to 2 per cent Zn, while the maximum tensile strength occurs between 8 and 10 per cent Al, and 1 to 2.5 per cent Zn. It should be noted that for the alloys improved by aging, both the yield and tensile strengths are raised considerably by the quenching and subsequent aging treatment compared with the normal air cooling and aging treatment. The percentage elongations for quenched and aged alloys are so nearly the same as for air-cooled and aged alloys that no additional figure is presented.

At 300°F.

For testing at 300°F., the test bars were surrounded by a small resistance-type furnace and held at 300°F. $\pm 2^\circ\text{F}$. They were heated to testing temperature, held for $\frac{1}{2}$ hr. and pulled. Alloys were tested as heat-treated and aged, since this is the most stable of the commercial conditions at the testing temperature. Tests have shown that normal aging causes 80 per cent of the expansion due to precipitation that will occur at 300°F. The properties at 300°F. of the Mg-Al-Zn alloys in the heat-treated and aged condition are given in Figs. 22-25, inclusive. The elongations in general are higher at 300°F. than at room temperature. At 10 and 2 per cent Zn the elongation drops to 2 per cent, which is approximately that found in the heat-treated and aged alloys at room temperature. Fig. 22 shows two regions of maximum elongation, one at about 2 per cent Al, the other at about 6 per cent Al and 2 per cent Zn.

The yield strengths given in Fig. 23 have decreased because of the temperature rise to a point where they are about equal to the values for solution-heat-treated bars.

The maximum tensile strength at 300°F., as shown in Fig. 24, occurs at about 7 per cent Al and 2 per cent Zn as compared with the maximum room-temperature tensile strength occurring at about 9 per cent Al and 2 per cent Zn.

The Brinell hardness at 300°F. as shown in Fig. 25 shows no maximum or minimum points. The hardness gradually rises with increasing alloy content.

DISCUSSION OF RESULTS

A recent publication⁹ has presented information on the tensile properties and porosity characteristics for the same system of alloys covered in this paper. The data on porosity tendency agree well with the results reported here, while those for tensile properties are consistently lower. Two differences in technique may account for this. The English work was concerned with the true ternary alloys, while that reported in this paper was on alloys containing a few tenths of a per cent of manganese. In addition, the test bar used by Fox was the standard English type of bar (D.T.D. specification for sand-cast test bar) which produces consistently lower tensile properties than the design used in this country.

The commercial alloys listed in Table 1 can be evaluated in the light of the data presented. As pointed out earlier, the alloys now in use should be regarded not as individual alloys but as members of the Mg-Al-Zn system with a small amount of manganese added. Therefore, many of the properties are interdependent and all change in a gradual manner from one alloy to another.

On the basis of tensile strength, the casting alloys, H, C, A, G, Ag, and A10 fall either within, or very close to, the maximal limits defined in Figs. 16 and 19 for the heat-treated, and heat-treated and aged states, respectively. The AZ31 and AZF alloys, on the other hand, take advantage of the maximum ductility and tensile strength to be found in the as-cast state as shown in Figs. 12 and 14, respectively.

Within the group of heat-treatable alloys—namely, H, C, A, G, Ag, and A10—a further choice can be made based on porosity tendency, ease of heat-treatment,

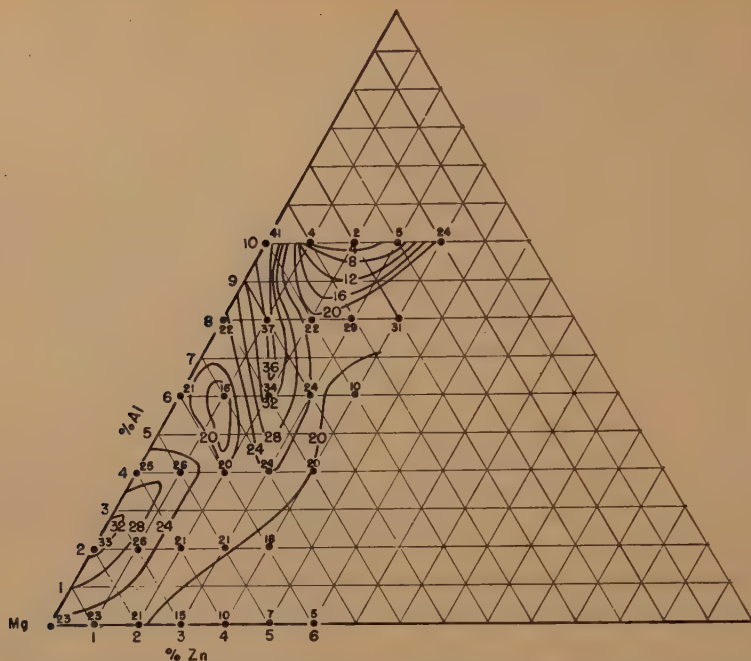


FIG. 22.—PERCENTAGE ELONGATION IN 2 INCHES AT 300°F. HEAT-TREATED AND AGED.

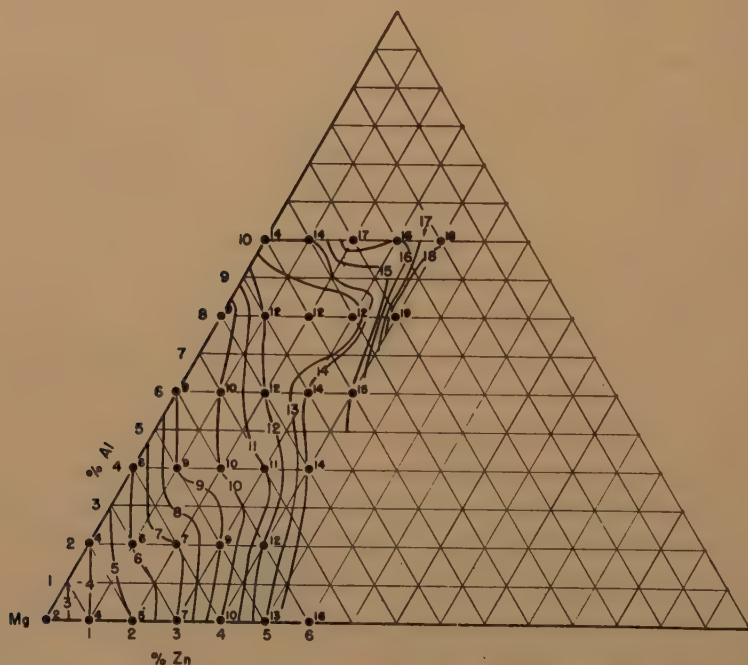


FIG. 23.—YIELD STRENGTH AT 300°F., 1000 POUNDS PER SQUARE INCH. HEAT-TREATED AND AGED.



FIG. 24.—TENSILE STRENGTH AT 300°F., 1000 POUNDS PER SQUARE INCH. HEAT-TREATED AND AGED.

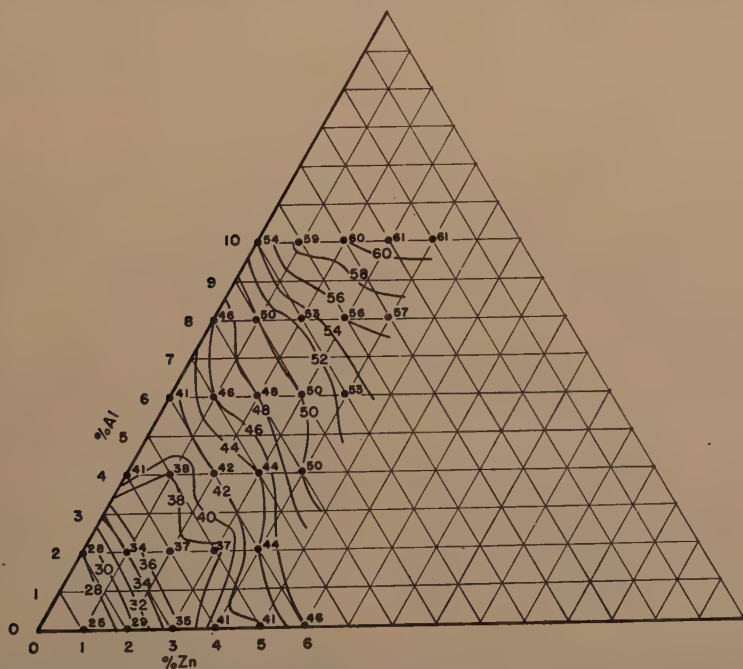


FIG. 25.—BRINELL HARDNESS NUMBER AT 300°F. (500-KG. LOAD AND 10-MM. BALL). HEAT-TREATED AND AGED.

germination tendency, and possibly fluidity and shrinkage.

The low-zinc alloys such as A, G, Ag, and A10, show a lower porosity tendency than the higher zinc alloys as indicated in Fig. 7. C alloy is somewhat of a compromise between the low-zinc and high-zinc alloys in respect to porosity tendency.

H alloy has the advantage of greater ease of heat-treatment (i.e., shorter time at the heat-treating temperature) than the alloys with a greater total alloy content. H alloy also has the advantage of being outside the germination range.

Other considerations, such as corrosion resistance and toughness, which have not been covered in this paper but which have been discussed in a previous publication,¹ may also influence the choice of an alloy.

SUMMARY

Comprehensive data have been presented on various properties of magnesium-rich sand-cast Mg-Al-Zn alloys. The data, which have been presented in graphical form, include constitutional, casting, and mechanical properties.

The various graphs show optimum properties at different compositions. It is, therefore, necessary to select a particular alloy composition that will include the desired properties for a particular application.

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DISCUSSION

(J. D. Hanawalt presiding)

R. J. RAUDEBAUGH.*—I should like to ask the speaker if he would describe the method used in casting the porosity test piece.

R. F. MARANDE (author's reply).—The reference given in the body of the paper quite thoroughly discusses the type of panel used in the porosity measurements. A sketch showing the dimensions of this panel is reproduced here (Fig. 26). In this work the panel was attached to the regular test-bar pattern and poured with the test bars. The gate was cut off flush with the long section of the panel, giving a bar $10\frac{1}{4}$ in. long by $1\frac{1}{2}$ in. wide to be radiographed.

H. Y. HUNSICKER.†—Have you been able to draw any sort of correlation between the susceptibility to the unsoundness and the solidification temperature range in this particular series of alloys under the nonequilibrium solidification condition?

R. F. MARANDE.—There has been some discussion in the literature on this subject and we have given it considerable thought. However, it is difficult to explain the maximum and minimum points found in the porosity study on the basis of the length of the solidification range because the latter increases in a regular manner with increasing alloy content. It is quite probable that the solidification range is not the only governing factor. The proportions of liquid and solid present at a given point in

* Division of Engineering, University of Rochester, Rochester, New York.

† Aluminum Company of America, Cleveland, Ohio.

the solidification range may also have some effect.

J. R. LONG.*—I'd like to ask the authors to explain the test bar a little more fully—that is,

sents a useful contribution to our fundamental and technological knowledge of the magnesium-rich portion of the magnesium-aluminum-zinc system. The authors should be commended

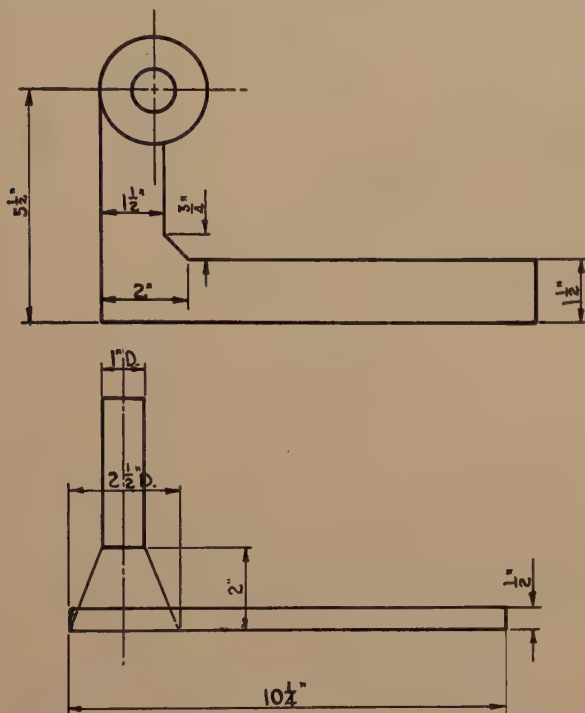


FIG. 26.—DIMENSIONS OF PANEL.

the mold, and so on—and also define what they mean by yield strength.

R. F. MARANDE.—The test bars were cast in a sand mold containing either four or six bars. The bars are about 6 in. long, with a reduced section $2\frac{1}{2}$ in. long and $\frac{1}{2}$ in. in diameter.

The yield strength is defined as the stress at the point where the stress-strain curve deviates 0.2 per cent from the modulus line. It is measured by determining the stress at 0.5 per cent elongation under load. This value is converted to the defined yield strength by an empirical relationship. The error in this method is about plus or minus 500 lb. per sq. inch.

L. A. CARAPELLA.†—This investigation, by its scope and painstaking character, repre-

sents a useful contribution to our fundamental and technological knowledge of the magnesium-rich portion of the magnesium-aluminum-zinc system. The authors should be commended

for the wealth of information they have supplied. The over-all treatment is, of course, concise, but there are a few instances where brevity of experimental details might render certain information somewhat misleading. Particular reference is made to both the fluidity and Brinell hardness tests, concerning which I should like to discuss and supplement in the light of work we have done at Mellon Institute.

According to the authors, a conventional spiral-type fluidity mold was employed for their fluidity test, reference being made to a publication by Saeger and Krynitsky.⁵ The pattern for the spiral fluidity test mold, as developed at the Bureau of Standards by the latter authors, was designed so that the molten metal in the pouring basin was fed down the center of the mold and to the outermost point

* Bureau of Mines, Salt Lake City, Utah.

† Metallurgist, Mellon Institute of Industrial Research, Pittsburgh, Pennsylvania.

on the spiral by means of a horn gate.* Special attention is directed to this feature because our experience with the originally designed pattern has revealed that with magnesium and

tion by Carapella and Shaw.¹⁰ The spiral fluidity curves for magnesium and a number of its alloys in the sand-cast condition are shown in Fig. 28. The difference between tests made on

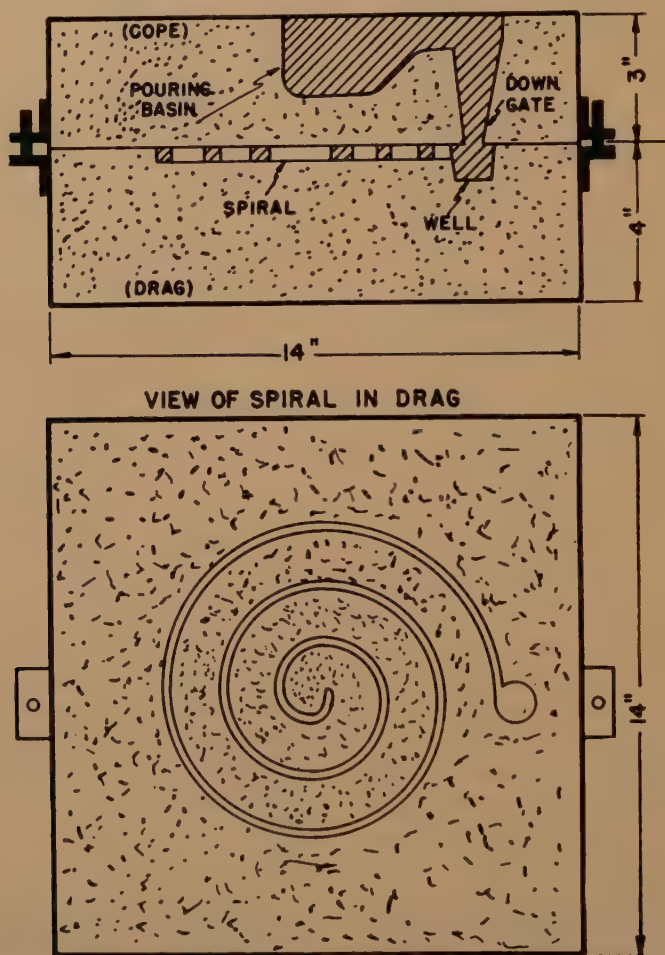


FIG. 27.—SCHEMATIC DRAWINGS OF A MODIFIED BUREAU OF STANDARDS SPIRAL FLUIDITY TEST PATTERN.

its alloys a better sensitivity is gained by omitting the horn gate and moving the down-gate to the position shown in Fig. 27. The details of the modified pattern and data to be presented have appeared in an earlier publica-

tion by Carapella and Shaw.¹⁰ The spiral fluidity curves for magnesium and a number of its alloys in the sand-cast condition are shown in this figure. Another feature to be noted here is the linearity of the data over the range investigated.

Along with the relative spiral fluidity per-

* Our fluidity test pattern, designed after the one of Saeger and Krynitsky, was purchased from Harry W. Dietert Co., Detroit, Michigan.

¹⁰ L. A. Carapella and W. E. Shaw: The Fluidity Performance of Magnesium Alloys. *Light Metal Age* (Nov. 1945) 3, 35.

formance of magnesium and its alloys, a comparison between our results and those of the authors is made in Table 2. It appears therefrom that the authors might have employed

about a 5-in. spiral flow at 1400°F. compared with their value of 25 inches.

Another fact concerning these tests as applied to magnesium alloys is that the venting

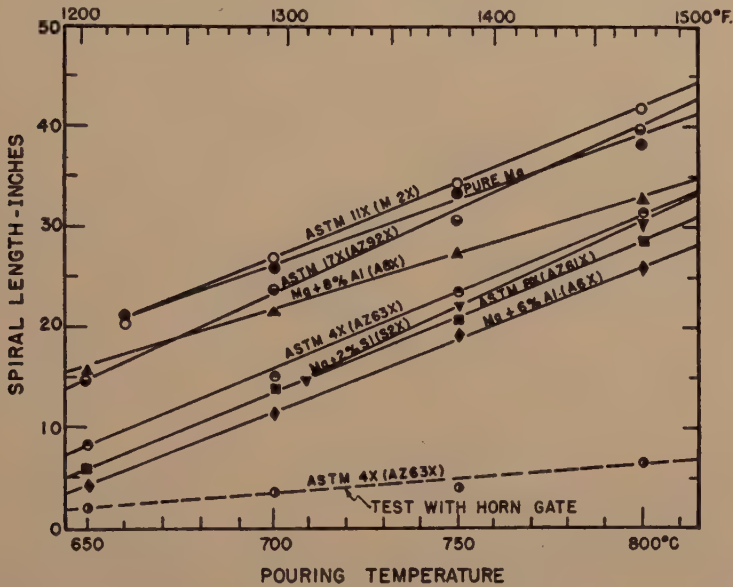


FIG. 28.—SPIRAL FLUIDITY CURVES FOR MAGNESIUM AND ITS ALLOYS IN SAND MOLDS.

a modified pattern similar to the one given in Fig. 27, instead of the original pattern with the horn gate as implied by their source of reference. Should this inference be contrary to actuality, we would appreciate learning more about the authors, pattern design and experimental procedure for conducting this test, because our data with the horn gate demonstrated A.S.T.M 4X(AZ63X) alloy to have

of molds at the end of the spiral, as suggested by Saeger and Krynsky, is unnecessary, for the green-sand permeability of around 100 to 160 is sufficient to permit an easy escape of generated gases without affecting the fluidity. One of the most important variables in our tests was the pouring technique. The manner with which the pouring basin was filled and the speed with which the metal was poured had

TABLE 2.—Relative Spiral Fluidity Performance of Magnesium and Its Alloys

Alloy Type	$S = \frac{\Delta L}{\Delta t}$		Pouring Temperature for a 25-in. Spiral Length		Spiral Length for 200°F (111°C.) above Liquidus Temperature, In.	Spiral Length for 1400°F. (760°C.) Pouring Temperature, In.	
	In. per Deg. F.	In. per Deg. C.	Deg. F.	Deg. C.		Carapella and Shaw	Busk and Marande
Pure magnesium.....	0.072	0.13	1274	690	34	34	30
A.S.T.M. 4X(AZ63X).....	0.083	0.15	1400	760	19	25	25
A.S.T.M. 8X(AZ61X).....	0.083	0.15	1430	777	17	22	19
A.S.T.M. 11X(M2X).....	0.083	0.15	1270	688	35	36	
A.S.T.M. 17X(AZ92X).....	0.095	0.17	1310	710	24	33	30
Mg + 2% Si(S2X).....	0.095	0.17	1414	768	33	24	
Mg + 6% Al(A6X).....	0.083	0.15	1463	795	17	20	23½
Mg + 8% Al(A8X).....	0.061	0.11	1346	730	23	28	18½

considerable influence on the results. The initial overflow of molten metal from the basin into the downgate had to be continuous and rapid; otherwise, any splashover into the downgate from poor technique would retard the flow. Contrariwise, very slow pouring would cause an appreciable drop in the metal temperature, thereby producing low fluidity values. With proper pouring, our results from a number of test runs on a given alloy for a related pouring temperature rarely exceeded one inch from the average value. Of all the foundry methods used to ascertain the relative castability of metals, we feel the spiral fluidity test is superior; and for most nonferrous metals, we recommend the modified Bureau of Standards spiral fluidity test pattern.

The presentation of Brinell hardness values at 300°F. for alloys in the heat-treated and aged condition provides some interesting data, but the room-temperature values should have been included also for comparison. Furthermore, these hardness values would yield more significance if the load duration were indicated along with the testing load and ball diameter. That load duration has a profound influence on the Brinell hardness of magnesium has been revealed in our recent investigation of factors affecting hardness.¹¹ Some of our unpublished data are set forth in Table 3 to point out the effects of load duration on the Brinell hardness of magnesium under several testing loads. Of importance is the fact that all listed Brinell numbers were calculated from impression diameters having d/D values within the specified limits of 0.25 and 0.6.* Therefore the Brinell hardness numbers for magnesium at room temperature may rightfully vary; for example, between 27 and 41. This condition clearly illustrates that hardness thus measured is not a fixed parameter by which to define the physical state of the material, but, instead, is a measure of the inherent nature of the metal per

se and the extent of plastic deformation sustained during test at room temperature. At elevated temperatures the load-duration factor becomes much more important, for plastic flow rates are greatly augmented. Consequently, to attach any definite significance to Brinell hardness numbers, it is imperative to state the necessary testing variables, such as ball diameter, load, time, and temperature; accordingly, $H_{10/500/180} = 34.8$ (at room temperature).

R. F. MARANDE.—Mr. Carapella is correct in pointing out that the spiral fluidity test mold used by Saeger and Krynsky has been modified for use with magnesium and magnesium alloys. In the modified version the downgate connects with the outside of the spiral and the horn gate is eliminated. It was the modified fluidity mold that was used in this work.

TABLE 3.—*Brinell Hardness Values at Room Temperature for Extruded Magnesium Rod, Average Grain Size 0.0010 Millimeters*

Load Duration, Sec.	Testing Load, Kg.			
	250	500	750	1000
15	33.4	37.8	40.6	40.8
30	32.2	37.0	39.7	40.1
60	31.1	36.1	38.6	39.5
120	30.0	35.2	38.1	38.7
180	29.4	34.8	37.5	38.4
300	28.7	34.1	37.0	37.8
600	27.7	33.3	36.2	37.2
1000	27.1	32.8	35.7	36.7

We agree with Mr. Carapella's results concerning the linear relationship between fluidity as measured by the spiral test mold and the temperature. However, we do not feel that this spiral test can be used entirely to predict the relative castability of magnesium alloys in the sand foundry because the term castability includes such factors as freedom from cold shuts, cracking and draws.

The load duration of the Brinell hardness determinations was 30 seconds.

¹¹ L. A. Carapella and W. E. Shaw: Factors Affecting the Technical Hardness of Magnesium. (On press.)

* These limits have been specified to overcome the shortcomings of the Brinell test at higher loads or at greater impression diameters.

Preparation and Properties of Ductile Titanium

By R. S. DEAN,* J. R. LONG,† F. S. WARTMAN‡ AND E. L. ANDERSON†

(Chicago Meeting, February 1946)

TITANIUM has been estimated to comprise about 0.65 per cent of the earth's crust and ranks fourth in abundance among the metallic elements suitable for engineering uses. In spite of this, applications of titanium for structural purposes have not as yet been developed. Its commercial exploitation has been largely confined to the chemical industries and the production of paints and pigments; no doubt because of the difficulties that lie in the way of preparing the pure ductile metal. Published reports, however, indicate that ductile titanium can be prepared and possesses some unique properties. This, together with the occurrence in this country of several important titaniferous deposits, has led the Bureau of Mines to investigate processes for the production of metallic titanium, methods required for its fabrication, and the properties that may be produced in this interesting metal.

METHODS OF PREPARING METALLIC TITANIUM

Many early investigators claimed to have isolated metallic titanium; but in the light of present knowledge, it seems that

Manuscript received at the office of the Institute July 26, 1945. Issued as T.P. 1961 in METALS TECHNOLOGY, February 1946.

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they really had produced various mixtures of carbides and nitrides that have a metallic appearance but are brittle, hard, and unworkable. The first metallic titanium pure enough to be malleable when cold was produced by Hunter¹ in the early part of the twentieth century. Kroll,² van Arkel,³ and Fast,⁴ subsequently confirmed the facts that pure titanium is a ductile metal and that small amounts of impurities were responsible for previous reports of brittleness.

When heated, titanium reacts chemically with various gases, such as hydrogen, oxygen and nitrogen; if the volume of gas thus absorbed is too great, the metal becomes brittle and unworkable. The principal difficulty in making ductile titanium is prevention of such contamination, and the success of a given process may be judged by the completeness with which it solves this difficulty in a practical manner.

Of the gases mentioned, hydrogen is the least objectionable, since its absorption by the metal is completely reversible and, although dimensional changes occur and absorption of hydrogen embrittles the metal, the gas may be removed readily by heating in a high vacuum for a short time.

On the other hand, the absorption of oxygen or nitrogen results in the formation of permanent solid solutions of the oxide and nitride, which cannot be decomposed by the strongest reducing agents² with sufficient completeness to restore the inherent ductility of the metal. Because of

¹ References are at the end of the paper.

this, it has thus far been possible to prepare ductile titanium only in an environment substantially free from nitrogen, oxygen and the compounds of either.

Two methods of producing metallic titanium pure enough to be ductile at room temperature are available at present. One, developed by Van Arkel and co-workers^{3,4,5} at the Philips' works in Holland, involves thermal decomposition of titanium iodide on a heated surface, whereby metallic titanium is deposited on the surface and iodine is liberated as a gas. This technique gives titanium that contains a minimum of dissolved gas and is therefore quite ductile, but it suffers from three defects. In the first place, it is essentially a method of purification rather than production, since low-grade metallic titanium is required as a raw material; second, it would be quite difficult to adapt the technique to large-scale production; and third, the metal is produced in pencil-shaped rods, which cannot be melted into larger lots without contamination.

The other method involves reduction of titanium tetrachloride by a more active metal and yields titanium in a granular or powdered form more readily adapted to subsequent consolidation. The Hunter¹ process uses sodium and the Kroll⁶ process fused magnesium. After considering virtually every process proposed for the production of metallic titanium and investigating the Van Arkel, Kroll, electrolytic, and several other processes, it was concluded that the Kroll process was the most practical for large-scale operations.

Briefly, this process consists of the reduction of titanium tetrachloride with magnesium at a temperature of about 800°C. The reaction mixture, consisting of titanium, magnesium chloride, and unreacted magnesium, after cooling, is crushed and leached. The resulting granular titanium is ground wet, re-leached to remove the magnesium, dried, and con-

solidated by powder methods or by a special arc process.

EXPERIMENTAL WORK

A diagrammatic sketch of the apparatus used in the preliminary studies is shown in Fig. 1; the details, functions, and its various parts are self-explanatory.

The weight of titanium produced per batch is determined by the size of the reduction pot, which at first was about 1¼ in. in diameter and 2 in. high. This, although small, was sufficient for the initial purpose. The Kroll technique was followed, except for the method of cleaning and preparing the reduction chamber for each run. This procedure consisted of heating the reduction chamber to a temperature of about 500°C. in an atmosphere of hydrogen, completely reducing any iron oxide present, then replacing the hydrogen with helium that had been purified previously by passing over activated charcoal cooled with liquid air.

The chamber was then loaded with carefully cleaned pieces of magnesium, evacuated, filled with purified helium, and heated to about 750°C. by induction. After reaching the proper temperature, the titanium tetrachloride was allowed to drip onto the molten magnesium in the reaction chamber. During the addition of titanium tetrachloride, the temperature was allowed to rise gradually to about 1000°C., usually reaching this point at the time that all of the titanium tetrachloride had been added. On completion of the run, the pot was allowed to cool with its contents protected from oxidation by the helium atmosphere. The reaction mass was then dug out of the pot, mixed with cold dilute hydrochloric acid, ground, and re-leached to obtain a minimum of residual magnesium. On this first apparatus, the titanium yield was about 70 per cent and the magnesium efficiency about 60 per cent.

The titanium powder produced was compacted into small pellets at a pressure of

100 tons per square inch and sintered at 1000°C. in a high vacuum. After this treatment the compacts were usually malleable enough to withstand considerable cold

found both necessary and desirable. One of these was the use of an unlined iron pot instead of the molybdenum-lined pot initially used. Difficulties caused by molten

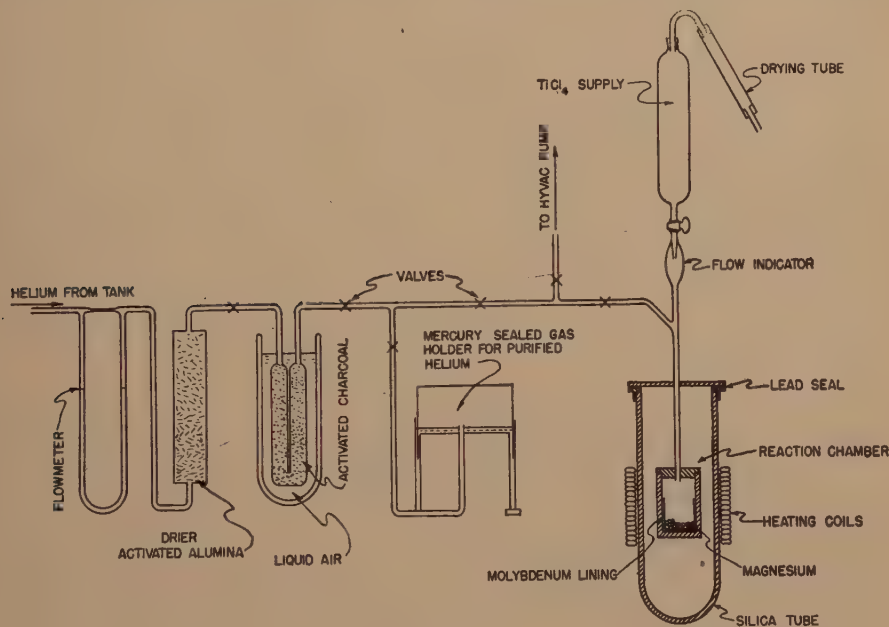


FIG. 1.—APPARATUS FOR SMALL REDUCTIONS.

deformation. Some of these pellets were rolled into strips 0.027 in. thick with intermediate annealing after about 20 per cent reduction in thickness with a final cold reduction of 50 per cent. The cold-worked strip was found to have a tensile strength of 101,000 lb. per sq. in. and a Rockwell hardness of 85 on the 30-T scale. When fully annealed, the strength dropped to 81,500 lb. per sq. in. and the hardness to 68.

These preliminary tests on the properties, combined with amenability to cold deformation, were sufficiently encouraging to justify considerable expansion in the scale of the work, and the size of the reduction apparatus was increased stepwise to a pot size capable of producing 15 lb. of titanium per batch.

In the course of this expansion, various changes in apparatus and technique were

material getting between the pot and the lining, and the lack of a satisfactory means of lining the larger pots, led to trial runs without the lining. The titanium produced in these runs was found to be quite satisfactory, and as long as the temperature did not rise much above 900°C. in the course of the run, the finished powder could be held to less than 0.1 per cent iron. Higher reaction temperatures resulted in a decided increase in the iron content of the final powder. This use of unlined pots accordingly restricted temperature to the narrower range of 750° to 900°C. Purification of tank helium also became impracticable for the large apparatus and, although tank helium contains about 1.5 per cent nitrogen, it was possible to use it directly without purification, since the helium atmosphere in the reduction chamber is static and the

limited quantities of nitrogen thus introduced with the helium would not be enough to cause appreciable harm to the titanium.

hydrogen, to reduce the oxide formed on the interior surfaces by the welding. After cooling, 20 lb. of carefully cleaned magnesium ingots was introduced through the

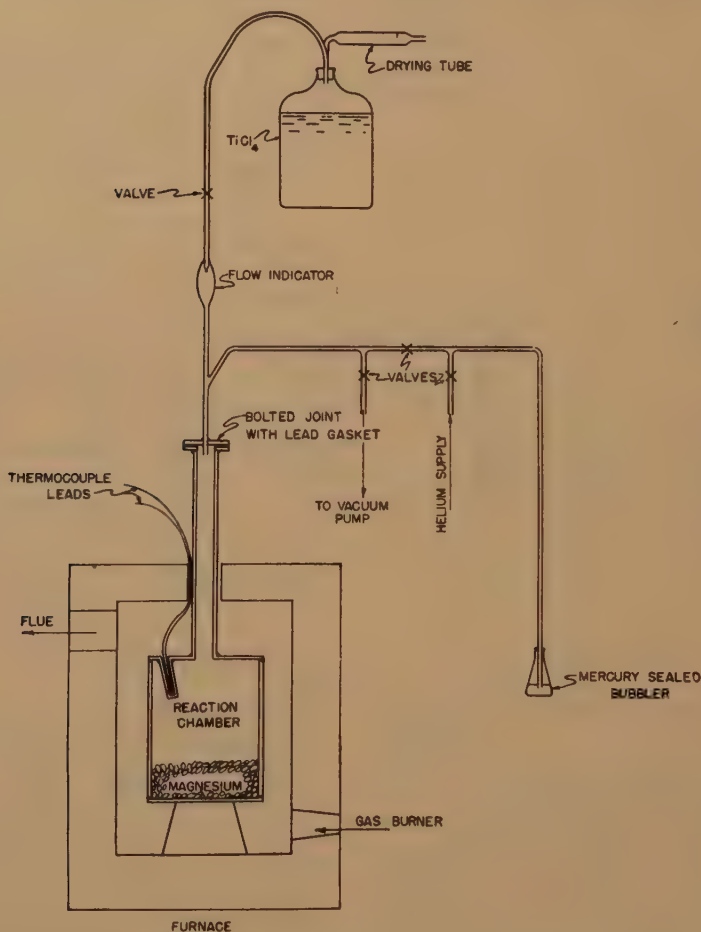


FIG. 2.—REDUCTION UNIT FOR 15-POUND RUNS.

The apparatus finally adopted for the 15-lb. runs is shown diagrammatically in Fig. 2. The pot, 12 in. in diameter and 14 in. high, was made from 12-in. pipe with $\frac{3}{8}$ -in. plates welded on the ends. The inside surfaces of the pot were carefully cleaned by pickling in dilute HCl, scraping, and finally polishing with an emery cloth. The cover was then welded on and the assembly heated to 500°C. while filled with

inlet tube and the assembly heated to 150°C., evacuating to a pressure of about 0.005 mm. mercury to remove absorbed gas from the walls of the chamber and the magnesium charge. Tank helium was next introduced, allowing the pressure to build up to slightly above atmospheric, and the temperature raised to about 750°C. The liquid TiCl_4 was run into the reaction chamber, slowly at first and then as

rapidly as the reaction would permit. The reaction of the TiCl_4 with the molten magnesium is exothermic, evolving about 2780 B.t.u. for each pound of titanium produced. This evolution of heat was sufficient, after the reaction got under way, to maintain the temperature of the chamber at the desired point without external heating for about two thirds of the run. In the latter portion of the run, no doubt because of the lack of magnesium available at the reaction surface, the rate of reaction decreased, reducing the rate at which TiCl_4 could be added; external heating then became necessary. The normal practice was to allow the temperature to rise gradually from an initial value of 750°C . to a final value of 900°C . and to maintain this temperature for about $\frac{1}{2}$ hr. after all the TiCl_4 had been added. Maintaining the temperature for this time at the end of the run was found to increase the size and toughness of the titanium particles in the reaction mass and this in turn reduced the proportion of very fine material in the product after leaching and grinding. During the entire run, a slight positive pressure of helium was maintained in the reaction chamber by means of the mercury valve indicated in Fig. 2.

LEACHING AND GRINDING

After the reaction chamber had cooled it was opened by cutting through the welded joint between the wall and the top of the pot. The charge was removed in the form of chips by a boring operation on a lathe. The greater portion of the magnesium chloride and excess magnesium was then removed from the chips by leaching with cold HCl . The leaching vessel was fitted with an agitator and cooling device, and the reaction chips were added at such a rate that the temperature of the leaching liquor did not exceed 25°C . Higher temperatures appeared to favor the formation of an undesirable film of oxidized material on the titanium particles and produced

hard metal with greatly reduced malleability. After the first leaching the chips were washed, dried, ground to the desired size, given a second leaching in 10 per cent HCl , and then carefully washed and dried at room temperature.

Several methods of grinding were tried. The material was easily ground notwithstanding the ductility of pure titanium; probably because of the absorption of hydrogen during the leaching. Initial lots from the smaller equipment were ground by hand in the steel mortar; later lots were ground in a small hammer mill, operating in the atmosphere of helium to prevent oxidation of the titanium particles. The heat generated by grinding was sufficient to set fire to the titanium when ground in air. Although the hammer mill worked well on this powder, wear was excessive, requiring frequent renewal of the screens. The final grinding method adopted was that of wet grinding in a small ball mill with frequent screening to remove the undersize particles and reduce the proportion of minus 200-mesh material produced. Although some iron was introduced by the grinding, it was readily removed by magnetic separation along with that picked up while the reaction mass was being bored out of the chamber.

EFFICIENCIES

The steps through which the size of equipment was increased up to that capable of producing 15 lb. of finished powder are indicated in Table 1, where the pertinent data characteristic of each stage are given. In general, very little difficulty was experienced in increasing the size of equipment; in fact, a number of advantages were obtained. Handling and measuring larger amounts of TiCl_4 were more convenient; the larger inlet tubes decreased the labor involved in cleaning the surface of the magnesium by permitting the use of larger pieces, and there was less spattering of the reaction mixture on the lids of the larger

chambers, decreasing the danger of the stoppage of the TiCl_4 inlet. There was no particular improvement in the leaching because the size of the leaching equipment was not increased commensurately with the increased size of the reduction apparatus.

of equipment. The figures given are based on the titanium added as TiCl_4 and the amount of usable powder obtained from it. The 20 per cent increase in efficiency between the smallest and largest batch is gratifying, and the 92 per cent efficiency

TABLE I.—Data on Reduction Process

	Bureau of Mines				Kroll
	1½	3½	6	12	
Size of reduction pot, in.	750-1000	760-850	740-820	800-870	740-1068
Temperature ranges, deg. C.	21 ^a	200 ^a	1,500 ^a	21.5 ^b	360 ^a
Magnesium used.	63.8 ^a	638 ^a	4,730 ^a	62.5 ^b	1,138 ^a
TiCl_4 added.	66	145	140	205	110
Time of TiCl_4 addition, min.	11.8 ^a	144 ^a	1,067 ^a	14.5 ^b	284 ^a
Titanium powder produced.	0.19	0.22	0.22	0.23	0.25
Ratio Ti: TiCl_4	73	89	89	92	98
Percentage of theoretical yield.	0.56	0.72	0.71	0.68	0.79
Ratio Ti: Mg.	57	73	72	69	80
Reduction efficiency of Mg, per cent.					

^a Grams.^b Pounds.

The reduction efficiency increased with increased scale of reduction but not quite to the extent expected. As shown by the data of Table I, the efficiencies, particularly those for magnesium utilization, were lower than those reported by Kroll. The rather low magnesium efficiency usually obtained in these reductions has generally been neglected. Investigation in these laboratories has shown that some of the magnesium is held between the grains of deposited titanium much as water is held in wet sand. Although no alloying appears to be involved, the adhesive forces apparently are strong enough to prevent the magnesium from rising to the surface of the reaction mass, where it can come into contact with excess titanium tetrachloride. It is possible to force the magnesium out by raising the temperature, but in an unlined reduction pot this would increase the iron content of the finished powder. The lower magnesium efficiencies obtained in this work are doubtless due to the lower reaction temperature. Other methods of increasing the magnesium efficiency are being studied.

The titanium efficiencies are also somewhat lower than Kroll's but, as previously noted, have improved with increased size

obtained in the 15-lb. batch, while quite satisfactory, can doubtless be further increased. However, all the factors involved are not controlled by the reduction; some titanium is lost in the iron-rich layer adhering to the wall of the reaction chamber, some in the leaching, and some as colloidal powder in the wash water. These losses may be minimized by close attention to the process, and particularly to the leaching conditions.

PRODUCT PURITY AND CONTROL

Maximum purity of the titanium was attained chiefly by control of raw materials used in the reduction. Initially, the small-scale runs were conducted with carefully purified TiCl_4 . In later work, with a larger apparatus, it was found impracticable to follow the usual purification procedures with the facilities then at hand, and chemically pure TiCl_4 commercially available was substituted. Qualitative tests indicated both kinds of TiCl_4 to be quite pure and no differences were noted in the titanium produced from either source. The magnesium used in the early work was redistilled Dow magnesium, but later high-grade commercial ingot metal was found to be quite satisfactory.

The finished powder produced by this technique is very similar in appearance to iron powder of a like size. Although it is somewhat sensitive to temperature during the leaching, apparently it is quite stable once the leaching process has been completed. Moist powder, if dried at high temperatures, will oxidize rapidly, covering the particles with a visible coating of the oxide. However, a sample of powder boiled for an hour in distilled water and then carefully dried produced metal that was essentially the same as a control sample made from the original powder. Other samples aged for several weeks in the laboratory atmosphere gave normal results when finally consolidated into metal strip. The fine, dry powder is inflammable and presents the same hazards as finely divided magnesium and other pyrophoric powders.

Precise analytical methods for determining small amounts of all of the impurities in titanium are not yet available, so it is not possible at this time to determine accurately the purity of the material produced. However, qualitative spectrographic examination permits some estimation of the metallic impurities present. In general, the same impurities found in magnesium were also present in the titanium. The chief impurities are iron, silicon, magnesium, oxygen, nitrogen, and hydrogen. The presence of the magnesium, as previously noted, is due to entrapment in the reaction mixture; although most of the unused magnesium can be removed by leaching, about 0.5 per cent escapes reaction with the leaching agent even after fine grinding, and remains in the finished powder. It is removed when the titanium is sintered at high temperatures and very low pressure; its presence in the powder is therefore not considered significant.

The iron is introduced by contamination in the reaction chamber, in boring the mix from the chamber and grinding of the final product. The free iron can be removed by magnetic separation, as can the major por-

tion of the titanium-iron alloy formed on the walls of the reaction pot. Complete removal is not attained, however, and some iron was found in all the powder produced. A reasonably accurate colorimetric method has been developed for determining this iron content. Briefly, the method consists of dissolving the sample in boiling sulphuric acid, oxidizing it to the quadrivalent form by the addition of nitric acid, and forming a colored iron complex by the addition of NH_4CNS . This complex is extracted with ether to avoid interference by the titanium, and the concentration of iron in the ether solution is estimated by comparison with appropriate standards in a suitable colorimeter. According to the results given by this method, the iron content of the titanium powder can be held easily below 0.1 per cent, and by very careful operation may be reduced to 0.03 per cent.

Silicon, while shown to be present spectrographically, did not appear to interfere with the malleability; therefore control of the silicon content was largely centered on preventing its introduction by the use of chemically pure TiCl_4 and high-grade magnesium. Preparation of spectroscopic standards for a determination of silicon is not yet complete. It is estimated that not more than 0.1 per cent silicon can be present in the finished metal.

In addition to the metallic impurities, the activity of the titanium with the various gases introduces a certain amount of the hydride, oxide and nitride. The hydride, as previously noted, is the least harmful, since the embrittlement produced by it is not permanent. The hydrides are decomposed and the hydrogen removed when the metal is heated in a vacuum. Measurement of the volume of gas thus evolved indicates that under the best conditions the powdered titanium contains 25 or 30 c.c. of hydrogen, at standard temperature and pressure, per gram of powder. It is absorbed as "nascent" hydrogen

evolved by action of the HCl on the excess magnesium. The hydrogen content of the powder may be greatly increased in the leaching if the temperature rises much above 25°C. or the acid concentration is too high.

Oxides and nitrides may be introduced at many points in the process even though special care is taken to exclude them. There are no direct methods for determining the amount of these constituents present, but their effects on the finished metal may be used as a means of control. Several experiments in which controlled amounts of oxygen were added to the powder in the form of TiO_2 showed that the pressed and sintered compacts increased in hardness in a regular and consistent manner with the increase of oxygen. Similar experiments with the nitride did not give conclusive results because of the slow diffusion of the nitride in titanium. However, comparison of the hardness of these compacts with the hardness of the metal produced by the Van Arkel process, under oxygen-free and nitrogen-free conditions, indicates that metal produced under normal conditions in these laboratories contained considerably less than 0.1 per cent combined oxygen and nitrogen.

POWDER METALLURGY

Since the product of this reduction technique was granular, it had to be consolidated before the metal could be utilized. Melting and casting of titanium presents many difficult problems; the metal has a high melting point and when molten reacts avidly with virtually everything with which it comes in contact. Available refractories are reduced by contact with the metal, which is then contaminated by both the oxide and the metallic element, and is embrittled. Kroll was able to melt the material on a small scale in a controlled atmosphere by a special arc melting process, which did not permit the molten metal to come in contact with anything but

titanium powder. His method, however, did not seem to be adaptable to the expanded operation contemplated. The methods of powder metallurgy, so successful with similar high-melting and active metals, were therefore employed.

The technique finally established involves the use of coarser metal powder and somewhat higher pressures than normally are used in powder metallurgy. These factors appear to be interrelated and controlled by the active nature of titanium. The fine powder, with its large surface area, becomes coated with a thin film of oxide upon exposure to the air, and the finer the particle size, the greater amount of oxide and hence the more brittle the compact formed from it. How much of this surface oxidation takes place in the leaching and how much in the drying is not yet clear. Fine powder, with its larger surface, produces unsatisfactory metal, and therefore is avoided as much as possible. Some fines, however, are necessary for proper compacting, in order to control the void space. Powder having a maximum particle size of 30 mesh with not more than 15 or 20 per cent minus 200-mesh was found to be a satisfactory compromise between the requirements of powder metallurgy and the great sensitivity of titanium to oxygen.

Titanium powder may be characterized as a soft powder. It presses well and the compacts may be handled freely without danger of breakage. The relationship between density of the green compact and the pressure is shown in Fig. 3, which gives data on compacts pressed up to approximately 100 tons per square inch. The increase in density with pressure is quite rapid up to 50 tons per square inch. Beyond this the rate of increase is considerably reduced. Since the gain in density with greater pressure did not appear to compensate for the disadvantages that the use of higher pressures involved, almost all of the compacts were pressed at 50 tons per square inch. At this pressure the com-

pression ratio of the powder is about $3\frac{1}{2}$ to 1. Some fragmentary data on the effect of lower compacting pressures on the properties of the finished metal indicate that the

this presents difficult problems in continuous purification of the helium. For work on a larger scale in the future, these problems may have to be solved, since

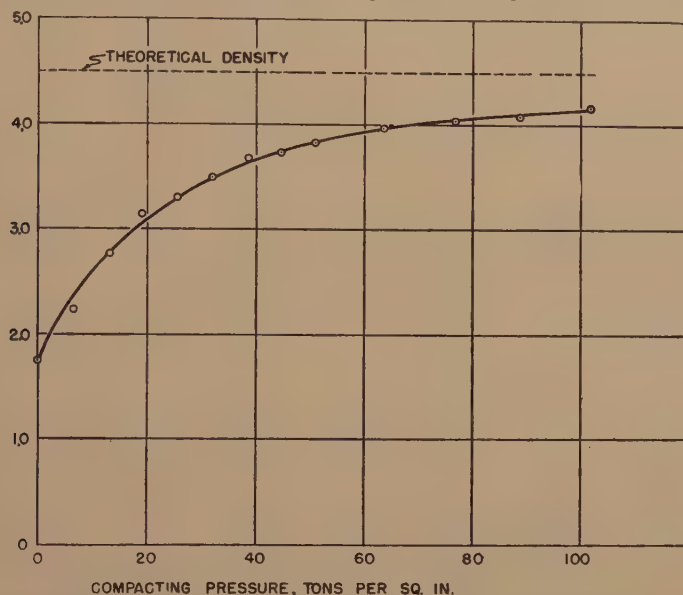


FIG. 3.—RELATION BETWEEN DENSITY OF GREEN COMPACTS AND COMPACTING PRESSURE.

best properties are obtained on compacts pressed at 50 tons per square inch. It is possible that lower pressures can be used when means of preparing finer powders without excessive oxidation are perfected, or when working schedules have been more fully developed for handling material with greater void space.

SINTERING

Sintering of titanium compacts requires a vacuum of the order of 1×10^{-4} mm. of mercury to remove the hydrogen absorbed during the leaching, to distill off residual magnesium, and to protect the metal from oxygen and nitrogen. An atmosphere of purified helium is not satisfactory because it does not permit the hydrogen and magnesium to be removed and the sintered compact is therefore brittle. While a current of purified helium at a few millimeters pressure would no doubt be satisfactory,

vacuum work at the required sintering temperature is also quite troublesome.

In sintering, the loss of hydrogen and magnesium give rise to a loss in weight, the void space is greatly reduced and the hardness of the compact increases. The effects of sintering temperatures from 600° to 1080°C. on these changes are given in Table 2 and plotted in Fig. 4. The data are based on a sintering time of 16 hr. at temperature. This sintering time was used as a standard, after a few trial runs at somewhat shorter and longer times were found to produce no significant differences in the sintered compact. This choice fitted the heating and cooling cycles of the sintering apparatus and permitted charging on one day, sintering overnight, and recharging the next day. Although this time was satisfactory for the immediate purposes, additional work will be necessary to establish the minimum sintering time.

The data show that weight loss and decrease of void space undergo the greatest change as the sintering temperature is increased; the volume of hydrogen evolved

because of insufficient consolidation while higher temperatures produced hard compacts difficult to work. Hydrogen may be completely removed above 600°C., but the

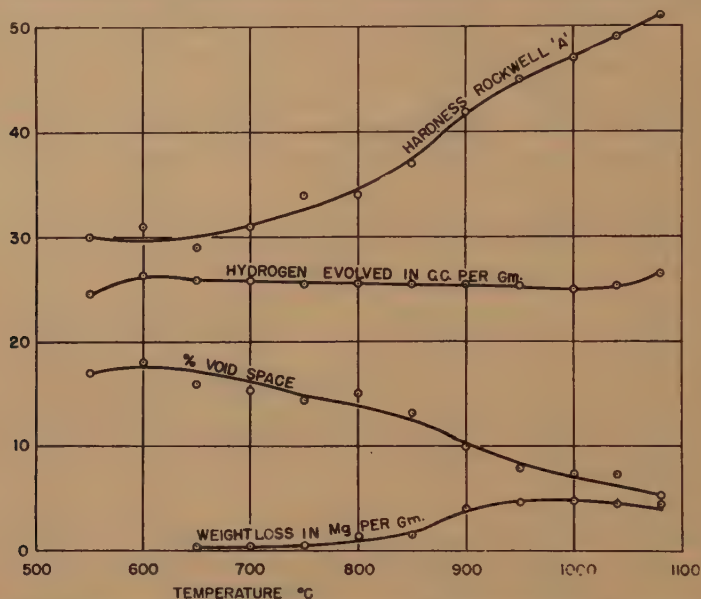


FIG. 4.—EFFECT OF SINTERING TEMPERATURES ON WEIGHT LOSS, VOID SPACE, HYDROGEN EVOLUTION AND ROCKWELL HARDNESS.

increases only slightly. Bonding of the titanium particles is also important but this is reflected in the ability to cold-work the compact. Compacts that could be

rate of evolution is very slow below 800°C. Loss of weight due to evolution of hydrogen and distillation of magnesium is small up to 850°C. and reaches a maximum at 950° to 1000°C. The change beyond this point is due probably to some oxidation of the titanium caused by increasing porosity of the sintering-furnace tube at the higher temperatures, masking the loss due to hydrogen and magnesium. The compacts sintered at 1100° and 1200°C. absorbed enough oxygen to decrease the malleability considerably; they were difficult, if not impossible, to cold-work. Void space decreased slowly with increasing sintering temperature up to 800°C. From 800° to 950°C. the decrease in void space was more pronounced. Higher temperatures showed little additional effects. Hardness reflecting the decrease in void space increased regularly for sintering temperatures from 700°

TABLE 2.—Sintering Data

Sintering Temperature, Deg. C.	Hydrogen Evolved, C.C. per Gram	Loss in Weight, Mg. per Gram	Void Space, Per Cent	Hardness, Rockwell A
550	24.5		17.0	30
600	26.3		17.9	31
650	25.9	0.38	15.8	29
700	25.8	0.44	15.5	31
750	25.5	0.65	14.5	34
800	25.5	1.17	15.2	34
850	25.5	1.50	13.3	37
900	25.4	4.05	10.0	42
950	25.3	4.83	8.0	45
1000	25.0	4.95	7.5	47
1040	25.4	4.59	7.5	49
1080	26.2	4.42	5.4	51

worked were obtained at sintering temperatures of 850° to 1000°C. Lower temperatures were found to be unsatisfactory

to 1080°C. From these data it is apparent that the optimum range in sintering temperature is 950° to 1000°C. Compacts sintered at these temperatures were ductile and could be readily cold-worked into thin strip.

FABRICATION

The main purpose of fabricating the pressed and sintered compacts was to check the amenability of the metal to plastic deformation; the hardness and ability to withstand cold-working by rolling and forging were the chief criteria. The working schedule was established early in the investigation and maintained throughout, so that the effect of changes in the process could be quickly evaluated.

Most of the working tests were run on small compacts 1 in. in diameter and about $\frac{3}{8}$ in. thick, although a number of $1\frac{1}{2}$ by 3 by $\frac{3}{8}$ -in., $1\frac{1}{2}$ by 3 by $\frac{3}{4}$ -in., and $\frac{1}{2}$ by $\frac{1}{2}$ by 6-in. compacts were also made and worked. The compacts usually were rolled into 0.025 to 0.030-in. strips, 8 to 10 in. long. Initial rolling reductions were carefully made at a rate of about 0.0015 in. per pass, the total reduction not exceeding 20 per cent before the first anneal. This anneal of 16 hr. at 1000°C. was in effect a second sintering and, like all of the annealing, was run in a high vacuum. On subsequent working the reductions per pass were tripled and the reduction between annealing increased to 30 or 40 per cent. The annealing temperature was lowered to 800°C. and the time to 2 hours.

Compacts were considered satisfactory if they could be finished into 0.025 to 0.030-in. strip with 50 per cent cold reduction without excessive edge cracking and without visible surface defects.

This fabricating schedule was quite effective as a means of checking the effects of the many variables in the process on the finished powder, and was used as a means of establishing the proper controls. All lots of powder produced and all variations in-

troduced in the process were checked by the results of the fabrication tests. The grinding, leaching, and drying techniques, in particular, were established on this basis, since excessive oxidation of the powder in these steps invariably produced hard compacts difficult to work. Oxidized powders usually could be salvaged by re-leaching and drying under proper conditions.

PROPERTIES OF TITANIUM

The density and hardness were determined on these compacts at all stages of fabrication in order to follow the changes that resulted from the working. The void space was about 14 per cent in the pressed compact, 7 per cent as sintered, 2 per cent after the initial working, and approached zero after the compact had been reduced to about 50 per cent of the as-sintered thickness. Normal cold-worked metal had a hardness of 60 to 70 on the Rockwell A scale and on annealing this dropped to 50 to 55. The as-sintered hardness was much lower, because of the high void space, and generally ran from A-40 to A-45.

TABLE 3.—*Properties of Metallic Titanium*

	Cold-worked	Annealed
Tensile strength, lb. per sq. in. . . .	126,000	82,000
Yield strength, lb. per sq. in. . . .	100,000	62,000
Proportional limit, lb. per sq. in. . .	72,000	55,000
Elongation, per cent in 2 in.	4	28
Young's modulus, lb. per sq. in. . . .		
$\times 10^6$	15.4	16.8
Hardness, Rockwell A.	65	55
Melting point, deg. C.	1,725	
Electrical resistivity, ohms per		
cu cm. $\times 10^6$	56	
Density, grams per c.c.	4.5	
Crystal structure up to 880°		
$\pm 20^\circ\text{C}$. hex. C.P.	$a = 2.95$ $c = 4.73$	
Above 880°C. B.C.C.	$a = 3.32$	

Tensile properties were determined on standard tensile specimens of 4-in. gauge length, cut from some of the strips. The values obtained were surprisingly consistent, considering that each specimen was made from a separate compact. However, there were significant differences from one lot of powder to the next as a

result of differences in the technique of processing, chiefly leaching and drying. Oxidized powders generally had higher tensile strength and lower elongation. Average properties representative of the usual run of the powder are given in Table 3. Some additional data on the melting point, transition temperature, and X-ray parameters as reported by Fast are also given. The cold-worked properties were obtained on strip reduced 50 per cent by cold-rolling after the last anneal; data for the annealed state were obtained on strips made from the same lot of powder similarly treated and annealed for 2 hr. at 800°C. after the cold-working.

RESISTANCE TO CORROSION

The corrosion resistance of titanium is very similar to that of 18-8 stainless steel. Corrosion tests on small strips with an area about 20 sq. cm. exposed to various corroding agents were conducted for two four-week periods to determine the rate of attack. The tests were run in tightly corked test tubes, to prevent loss of solution by evaporation, and the solutions were changed each week to ensure proper strength. Concentrated H_2SO_4 and HCl rapidly attacked the titanium but a 5 per cent H_2SO_4 produced a weight loss corresponding to only 0.40 mg. per sq. dm. per

TABLE 4.—Physical Properties after 30-day Salt-spray Test

Condition	Ultimate Strength, Lb. per Sq. In.	Yield Strength, 0.2 Offset, Lb. per Sq. In.	Proportional Limit, Lb. per Sq. In.	Modulus $\times 10^{-4}$, Lb. per Sq. In.	Elongation, Per Cent in 2 In.
Unexposed specimens:					
Annealed.....	73,400	50,900	44,400	13.5	25.9
Cold-worked.....	115,500	104,000	80,800	13.7	7.0
Exposed specimens:					
Annealed.....	73,500	53,900	48,900	15.0	25.3
Cold-worked.....	118,000	105,200	71,500	14.8	5.4

These are excellent physical properties and place titanium high in the list of strong, light metals. The yield strength and proportional limits are unusually high for an ultimate strength of 82,000 lb. per sq. in. and the 28 per cent elongation is indicative of good working qualities. Cold-working increased the tensile and yield strengths more than 50 per cent without complete destruction of the ductility. While this increase is not unusual for common metals, it is significant that titanium, with its hexagonal structure, can be worked to this extent at room temperature, and that such working produces large permanent increases in the tensile properties. The modulus of elasticity was determined by dynamic methods, which gave more consistent results than those obtained from tensile data.

Concentrated HNO_3 and 5 per cent solutions of HNO_3 , HCl, acetic acid, NH_4OH , and NaOH did not cause losses in excess of 0.05 mg. per sq. dm. per day. Another specimen in a dilute solution of sodium sulphide showed no weight change and was not discolored. Such resistance to chemical attack is quite surprising, considering the active nature of the metal, but probably is due to a protective film of the oxide, like those found on aluminum and chromium.

Exposure of both cold-worked and annealed specimens to salt spray for 30 days gave no visible sign of attack; the tensile properties remained essentially the same as those of control specimens made from the same lot of powder. Tensile properties obtained in this test are given in Table 4. These are average values for three speci-

mens in each condition and show no significant difference attributable to the exposure to salt spray.

Although finely divided metal is pyrophoric, the minus 35-mesh powder used in these investigations is quite stable. It may be ignited deliberately but does not ignite spontaneously. Titanium wire in sizes under 0.010 in. can be ignited in a Bunsen burner but in larger sizes it simply undergoes surface oxidation, coating the metal with an oxide scale. At higher temperatures some nitride is also formed.

SUMMARY

Laboratory investigation of the preparation of ductile titanium by reduction of TiCl_4 with magnesium has progressed satisfactorily up to the production of 15-lb. batches of titanium powder without encountering any technical difficulties that would prevent the expansion and use of this process on a large scale. The granular metal product is produced in a high state of purity, containing about 25 c.c. of hydrogen per gram of metal and 0.50 per cent magnesium, both of which are completely removed by sintering at 1000°C . in high vacuum. The powder may contain up to 0.1 per cent iron and a few tenths of oxygen as the oxide. No information is available on the silicon content, but it is believed to be less than 0.1 per cent. These latter impurities are not present in sufficient amounts to interfere with the ductility of the metal.

The powder has been consolidated by pressing into compacts at a pressure of 50 tons per square inch and sintering at 1000°C . in a vacuum of 1×10^{-4} mm. Hg.

These sintered compacts are ductile, lend themselves readily to cold deformation, and have been made into sheet and bar by normal fabricating methods. Annealed material has a tensile strength of about 82,000 lb. per sq. in. with 28 per cent elongation and a hardness of 55 on the Rockwell A scale. It is hardened by cold-working; tensile strength for 50 per cent reduction by cold-work is about 126,000 lb. per sq. in. with 4 per cent elongation and a Rockwell hardness of A-65.

The metal has excellent corrosion resistance, being very similar to the 18-8 stainless steels in this respect. It is rapidly attacked by sulphuric acid and hydrochloric acid; dilute sulphuric acid attacks the metal slowly but concentrated and dilute nitric acid have no appreciable effect. The metal does not tarnish on exposure to laboratory atmospheres or during a 30-day exposure to the salt-spray tests. Physical properties are also unaffected by salt-spray corrosion tests. The consolidated material is quite stable. It may be heated to at least 800°C . in air without taking fire.

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Ductile Titanium—Its Fabrication and Physical Properties

By R. S. DEAN,* J. R. LONG,† AND F. S. WARTMAN,‡ MEMBERS A.I.M.E., AND E. T. HAYES†

(Chicago Meeting, February 1946)

THE production of titanium in 15-lb. lots and with a purity sufficient to be consolidated into ductile metal, as described in a previous paper,¹ has provided adequate material for a study of the physical properties of titanium and a more thorough examination of its working qualities. Data on the physical properties reported in that paper were obtained on metal fabricated by a fixed procedure, standardized for the purpose of control of the reduction, and are representative only of material fabricated under those conditions. There are many possible variables in the working schedule, which will have significant effects on the properties of the finished material; and since the previous working methods were not necessarily the best, an investigation of the fabrication of titanium by other methods was undertaken. In this work the consolidation of the powder by pressing and sintering was conducted essentially as outlined in the report cited¹ and all efforts were centered on fabrication methods for those powders and the proper-

ties produced by them. Hardness, density, microstructure, and tensile properties were determined at various stages in the working and annealing; and resistivity measurements were made on a few bars and drawn wire.

TABLE I.—Screen Analysis of Titanium Powder

Tyler Sieve, Size	Weight, Per Cent	Cumulative Weight, Per Cent
+35	0.1	0.1
-35 + 48	25.0	25.1
-48 + 65	26.3	51.4
-65 + 100	17.4	68.8
-100 + 150	13.5	82.3
-150 + 200	7.5	89.8
-200	10.2	100.0

CONSOLIDATION OF THE POWDER

The screen analysis of the available titanium powder is given in Table I. No attempt was made to alter the size distribution from that noted because this powder, although coarse by normal powder-metallurgy standards, produced acceptable compacts suitable for the present work. Because of their large specific surface, finer powders are more contaminated by oxygen and produce harder compacts, which are difficult to work. The powder as produced is soft, compresses in a normal fashion, and exhibits very little tendency to adhere to the die surfaces. Unlike aluminum and magnesium powders, it can be readily pressed without the use of die lubricants. When compacted at 50 tons per

Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Manuscript received at the office of the Institute July 26, 1945. Issued as T.P. 1965 in METALS TECHNOLOGY, February 1946.

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¹ R. S. Dean, J. R. Long, F. S. Wartman and E. L. Anderson: Preparation and Properties of Ductile Titanium. This volume, p. 382.

square inch it has a compression ratio of about 3.5 to 1.

The compacts were pressed in a split die constructed in a manner that allowed

rated rapidly and therefore had no effect on the finished metal. It was used to simplify handling of the powder in loading and leveling and to help to reduce size segrega-

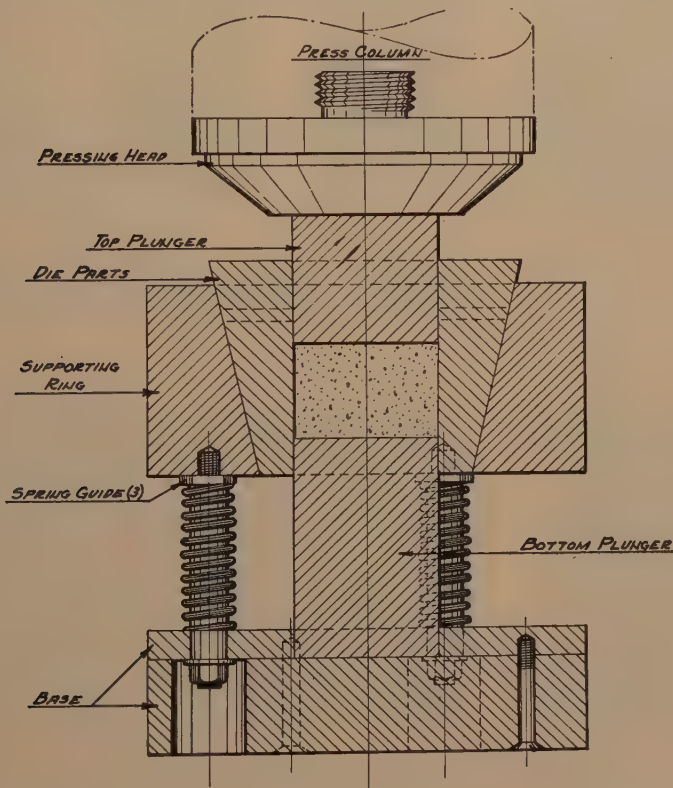


FIG. 1.—SECTIONAL VIEW OF DIE FOR PRESSING $1\frac{1}{2}$ BY 3-IN. COMPACTS.

distribution of the pressures on the top and bottom of the compact despite the use of a single-acting press. The essential features of this die are shown in Fig. 1, which is self-explanatory. Compacts $1\frac{1}{2}$ by 3 in. up to $\frac{3}{4}$ -in. thick can be produced in this die. A pressure of 50 tons per square inch was used for all this work and was found very satisfactory. The powder, moistened with C.P. benzene (about 5 per cent by weight), was loaded into the die in 50-gram increments, to reduce the tendency of the fines to segregate on leveling. About 95 per cent of the benzene was forced out of the powder in the pressing; the rest evapo-

tion. Most of the study was conducted on compacts $\frac{3}{8}$ -in. thick, weighing 100 grams, although a few compacts $\frac{3}{4}$ -in. thick weighing 200 grams, were prepared. These 100-gram compacts were best suited to the scale of these operations. For the bar and wire studies, a die designed to make compacts $\frac{1}{2}$ by $\frac{1}{2}$ by 6 in. was used. The compacts made and products fabricated from them are shown in Fig. 2.

The pressed compacts were sintered for 16 hr. at 1000°C . in high vacuum. A vacuum in the order of 2×10^{-4} mm. Hg was essential to remove the hydrogen and residual magnesium present in the raw

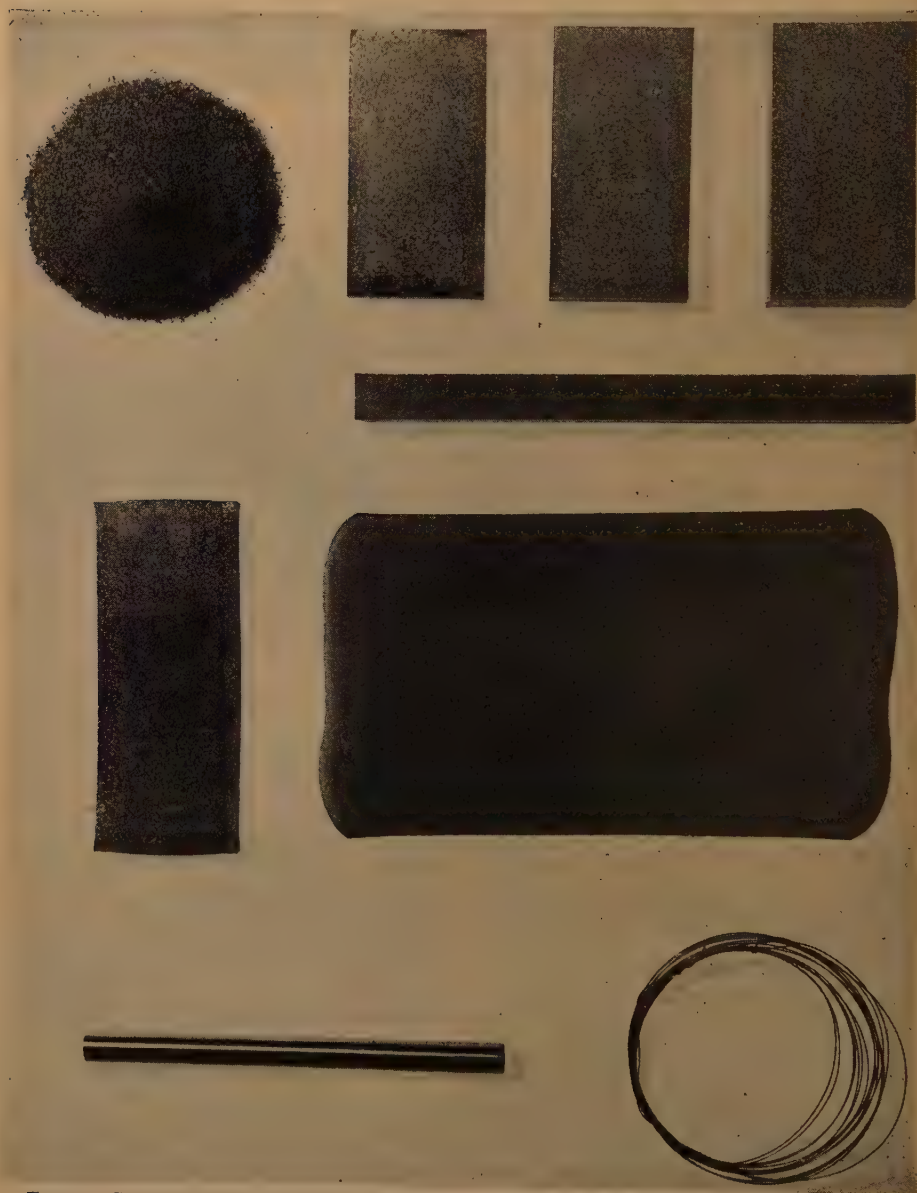


FIG. 2.—RAW TITANIUM POWDER, $1\frac{1}{2}$ by 3-IN. PRESSED AND SINTERED COMPACTS WEIGHING 100, 150, AND 200 GRAMS, FORGED AND ANNEALED 100-GRAM COMPACT, AND PROCESSED SHEET; $1\frac{1}{2}$ BY $\frac{1}{2}$ BY 6-IN. PRESSED AND SINTERED COMPACT, $\frac{3}{8}$ -IN. COLD-SWAGED ROD AND 0.020-IN. DIAMETER WIRE.

powder and to protect the titanium from oxygen and nitrogen, which react rapidly with the metal at the sintering temperature. Maintaining such a high vacuum at

Hg and carefully tested for leaks before heating. When the system was heated, evolution of hydrogen reduced the vacuum considerably but after 2 to 4 hr. at tem-

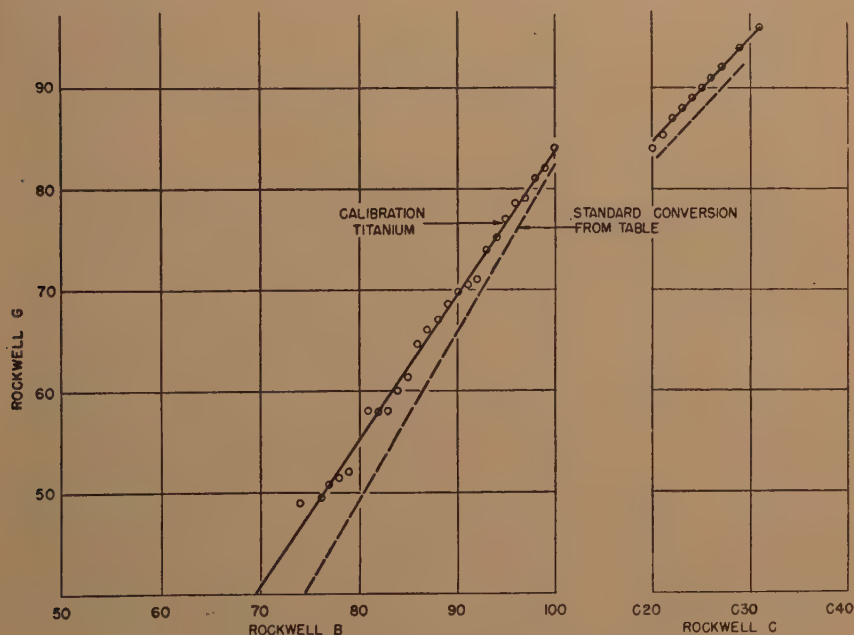


FIG. 3.—ROCKWELL CONVERSION CHART FOR TITANIUM METAL.

1000°C. was complicated by the great activity of the titanium present. It was necessary to take all possible precautions to avoid leaks in the system so that pressures measured would be representative of the true pressure in the system and not merely a reflection of the gettering action of titanium. McDanel porcelain tubes were found to be satisfactory for the sintering chamber and on blank runs at operating temperatures easily maintained a vacuum of 2×10^{-4} mm. Hg. A molybdenum tray inside the tube prevented contact of the titanium with the walls. The vacuum was obtained by a high-speed oil diffusion pump backed up by a mechanical pump. Suitable baffles were used in the system to minimize back diffusion of the oil.

In operation, the system was pumped down to a vacuum of 1 to 5×10^{-5} mm.

perature an ultimate vacuum of 2×10^{-4} to 5×10^{-5} mm. Hg was attained. On cooling, the vacuum was maintained until the metal reached 100°C. or less.

Shrinkage on sintering amounted to about 4 per cent of the linear dimensions and raised the density from 3.85 as pressed to 4.30 as sintered. The void space was correspondingly reduced from 14 per cent to 4 or 5 per cent. Loss in weight on sintering averaged about 0.80 gram for the 100-gram compact and was approximately equal to the sum of the hydrogen and magnesium present in the raw powder. The removal of this hydrogen and magnesium was necessary to obtain the maximum ductility of the titanium. Rockwell hardness of the sintered compact was G-52 to G-55. A few tensile tests on specimens of 0.125-in. diameter and $\frac{1}{2}$ -in. gauge length

gave a sintered strength of 83,000 lb. per sq. in. with 10 per cent elongation and a green strength of 3500 lb. per sq. in. with zero elongation. The as-sintered strength

with a black deposit, which is removed by vigorous swabbing, leaving a bright surface with the grain boundaries well delineated.

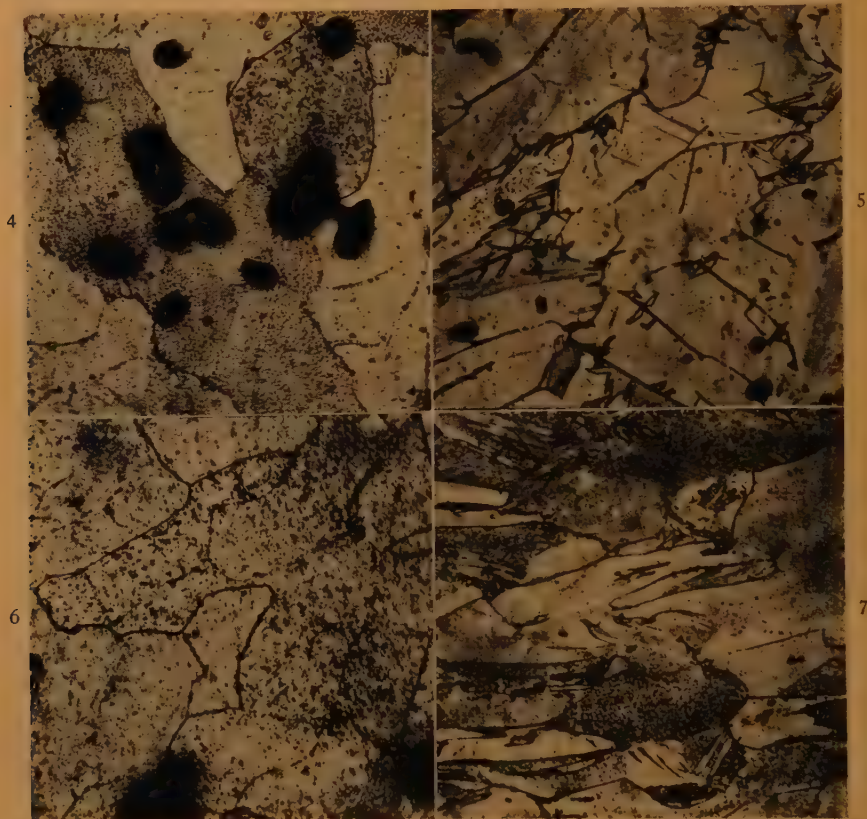


FIG. 4.—COMPACT VACUUM-SINTERED 16 HR. AT 1000°C. SLOWLY COOLED.

FIG. 5.—STRUCTURE OF COMPACT COLD-REDUCED 25 PER CENT BY FORGING.

FIG. 6.—STRUCTURE OF FORGED BAR AFTER VACUUM ANNEAL 6 HR. AT 1000°C.

FIG. 7.—SHEET COLD-ROLLED TO 40 PER CENT REDUCTION.

All $\times 250$.

was essentially the same as wrought material annealed at 1000°C. The elongation was lower, however, owing to the void space.

Fig. 4 shows the microstructure typical of the sintered material. It is a simple, polyhedral structure showing dark voids somewhat enlarged by the etching agent. A 5 per cent solution of hydrofluoric acid was found to be a very effective etching agent for titanium. It coats the specimen

FABRICATION OF SINTERED MATERIAL

The working methods previously used on the 1-in. diameter buttons were slow and tedious, particularly for the initial working stages, because of the relatively low ductility of the sintered material. The voids apparently interfere with the flow of the metal and necessitate light reduction and many passes. When heavy reductions are attempted, edge cracking becomes excessive and in some specimens

transverse surface cracks are developed. A reduction of 0.0015 in. per pass has been found to produce satisfactory results but a total reduction of 20 per cent at this rate is time-consuming.

Since hammer blows have a kneading action with greater depth and uniformity in effective working, as compared with the surface-layer working in rolling, particularly with light passes, cold-forging was adopted for the first forming stage. The forging was accomplished with a 100-lb. power hammer, using rounded dies to concentrate the force of the blow and assist in directing the flow of metal. The compacts were readily reduced by this method in much shorter time without danger of shear cracking. While reductions as high as 50 per cent in thickness were made in some tests, the danger of overwork made it desirable to standardize on a 25 per cent reduction. The forging of the compacts led to increase in the length from 3 to $3\frac{3}{4}$ in. and decrease of the thickness to about $\frac{1}{4}$ in. In this operation, the density increased from 4.30 to 4.42 (void space decreasing from 4.5 to 2.5 per cent) and the hardness increased from Rockwell G-54 to G-81. Tensile strength of small $\frac{1}{8}$ -in. tensile specimens cut from forged compacts showed a strength of 115,000 lb. per sq. in. with 6 per cent elongation. The microstructure of the forged bar is given in Fig. 5. Since this material has been reduced by only 25 per cent, the distortion of the grains is not great; there is, however, some twinning not evident in the annealed structure.

The forged compacts were given a 6-hr. vacuum anneal at 1000°C. This operation was considered both as a second sintering and an anneal, in that it promotes welding of the voids closed in the forging, homogenizes the structure and produces a product sufficiently soft for further treatment. The annealed metal has a density of 4.44—a slight, but definite, increase over the forged condition.

The hardness and strength dropped to the same level as those of the sintered compacts and the elongation increased to 19 per cent, twice that of the sintered material. The microstructure of this annealed material is given in Fig. 6 and shows fewer voids than in the sintered compact.

Through all subsequent processing of titanium in this study, the procedure of pressing, sintering, forging, and annealing was standardized as described previously; that is, pressing minus 35-mesh powder at 50 tons per sq. in.; vacuum sintering at 1000°C.; and cold-forging to 25 per cent reduction in thickness, followed by a 6-hr. vacuum anneal at 1000°C.

Some of the material was hot-rolled (500°C.) and some cold-rolled for comparison of the working and the effects of each on the physical properties. The metal was generally rolled into $\frac{1}{16}$ -in. sheet by schedules calculated to finish with varying degrees of reduction after the last anneal. Hardness, density, microstructure, and tensile properties were determined for various stages of working and on material annealed at temperatures from 400° to 1200°C. after working.

The tensile properties for the most part were determined on the $\frac{1}{16}$ -in. sheet, using standard specimens 0.5 in. wide with a total gauge length of 4 in. A few values representative of unfinished material were determined on round specimens with a $\frac{1}{8}$ -in. gauge length, $\frac{1}{8}$ in. in diameter. All the tensile specimens conform to A.S.T.M. standards for sheet and round stock.

The hardness was measured on the Rockwell G scale to cover the range involved with a single scale. Soft annealed material registered in the neighborhood of 75 on the B scale while cold-worked metal often registered above 30 on the C scale. Other Rockwell scales that cover a similar range involve the use of light loads and are subject to fluctuation because of the

voids present in the first few working stages. Conversion from the G scale to the B or C scale is best made by the graph of Fig. 3, which was drawn from values

per cent at a rate of 0.004 in. per pass. Metallographic examination of representative samples showed that this schedule produced essentially the same grain size

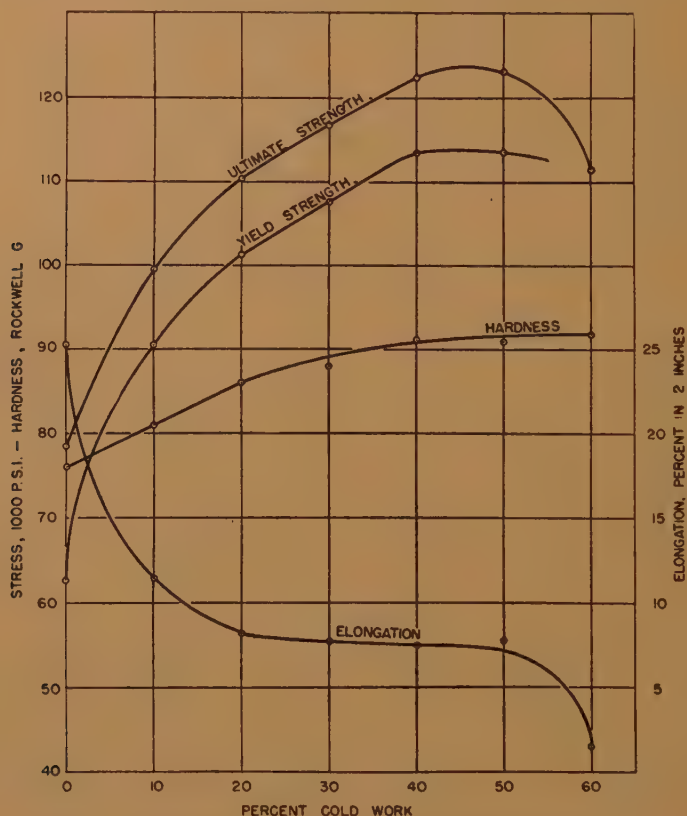


FIG. 8.—PHYSICAL PROPERTIES OF COLD-WORKED TITANIUM.

determined on the same piece using both scales. The standard tables give values 2 to 3 points high when used for converting from G to B or C hardness.

EFFECTS OF COLD-ROLLING

Half of the forged and annealed compacts were cold-rolled into $\frac{1}{16}$ -in. sheet with intermediate vacuum annealing at 800°C. as required. The cold-rolled material was finished with 10, 20, 30, 40, 50, and 60 per cent reductions after the last anneal. Intermediate reductions, prior to reaching the ready-to-finish size, were 15 to 20

after each annealing. The compacts were first rolled along the short dimension to give sheet about $2\frac{1}{4}$ in. wide and then lengthwise in order to produce sheet large enough to make three standard tensile specimens from each piece.

Physical properties obtained on the cold-worked sheet are given in Table 2 and plotted in Fig. 8 as a function of cold-rolling. The zero cold-worked condition is represented by material that had been cold-rolled to 40 per cent reduction and given a 2-hr. anneal at 800°C. All the

values listed are average of the results on six separate specimens.

TABLE 2.—*Tensile Properties of Cold-worked $\frac{1}{16}$ -inch Titanium Sheet*

Per-centage of Reduc-tion	Ulti-mate Strength, Lb. per Sq. In.	Yield Strength, 0.2 Off-set, Lb. per Sq. In.	Pro-portion-al Limit, Lb. per Sq. In.	Elonga-tion, Per Cent in 2 In.	Hard-ness, Rockwell G
0 ^a	78,700	62,800	56,600	25.2	76
10	99,500	90,500	65,300	11.5	81
20	110,500	101,100	76,900	8.2	86
30	116,900	107,600	81,100	7.7	88
40	122,200	113,300	84,400	7.5	91
50	123,000	113,500	83,300	7.8	91
60	111,500		86,600	1.5	92

^a 40 per cent cold reduction and annealed 2 hr. at 800°C.

The tensile strength increased from 78,700 lb. per sq. in. for annealed material to 123,000 at 50 per cent reduction and then dropped to 111,500 lb. per sq. in. at 60 per cent reduction. Yield strength shows a similar trend, reaching a maximum of 113,500 lb. per sq. in. at 50 per cent cold-

that 50 per cent cold reduction is the safe working limit under these conditions and that little is to be gained in increase of strength and hardness by working beyond 40 per cent reduction. Material for study of the effect of annealing temperature on the physical properties was finished with 40 per cent cold reduction and then annealed for 2 hr. at temperatures ranging from 400° to 1100°C. Tensile properties obtained on these specimens are given in Table 3 and Fig. 9.

The relationship between physical properties, microstructure, and annealing temperature follows the same general pattern of the common metals. The 122,200 lb. per sq. in. tensile strength for 40 per cent cold-worked sheet is decreased to 99,200 lb. per sq. in. by annealing at 400°C., and drops to 79,000 lb. per sq. in. on annealing at 700°C. Annealing at 800° and 900°C. does not alter the strength appreciably, but higher temperatures produce a definite increase. The tensile strength rises to

TABLE 3.—*Tensile Properties of Cold-worked and Annealed $\frac{1}{16}$ -inch Titanium Sheet*

Annealing Temperature, Deg. C.	Ultimate Strength, Lb. per Sq. In.	Yield Strength, 0.2 Offset, Lb. per Sq. In.	Proportional Limit, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Hardness, Rockwell G	Grain Size, Mm.
400	99,200	92,100	76,500	15.3	87	
500	90,700	81,300	71,100	18.5	87	
600	82,100	69,400	63,400	22.9	79	
700	79,000	64,700	59,500	25.2	78	0.025
800	79,100	64,000	58,800	24.7	76	0.035
900	78,500	65,000	58,000	23.8	77	0.045
1000	80,500	64,500	44,800	22.5	67	0.045
1100	81,500	65,400	41,100	21.5	68	0.090

work. Hardness increases regularly from G-76 for zero cold-work to G-92 for 60 per cent cold-work. The percentage of elongation drops rapidly from an initial value of 25.2 to 8.2 at 20 per cent cold reduction. It is substantially unaffected from here through 50 per cent cold-work but drops to 1.5 at 60 per cent cold-work. The sharp decrease of strength and elongation for material cold-rolled to 60 per cent reduction are indicative of over-working. It is apparent from these data

81,500 lb. per sq. in. on annealing at 1100°C. This increase was found also in early work with the 1-in. compacts and appears to be characteristic of higher temperature anneals. It is not reflected in the yield strength, which drops from 113,300 lb. per sq. in. as cold-worked to 64,700 for 700°C. annealing and does not vary significantly with increasing annealing temperature up to 1100°C. The proportional limit behaves similarly for annealing temperatures from 400° to 900°C. but

drops sharply for material treated at 1000°C. The percentage of elongation increases to a maximum of 25.2 for 700°C. annealing and then decreases gradually to

rapidly at 1100°C. (Fig. 15). The transformation of alpha to beta titanium on heating above 875°C. appears to have little or no influence on the resultant grain size.

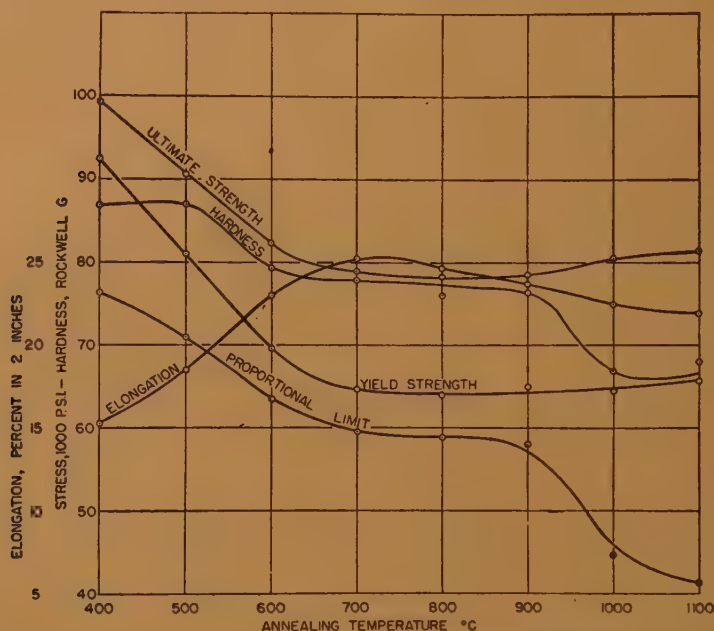


FIG. 9.—PHYSICAL PROPERTIES OF COLD-WORKED AND ANNEALED TITANIUM.

21.5 for an 1100°C. anneal. Hardness drops from G-91 as cold-worked to G-87 for 400°C. and to G-79 for 600°C. and remains at this value for other annealing temperatures up to 900°C. It is decreased to G-67-68 on annealing at 1000° to 1100°C.

The effect of annealing on the microstructure is shown in Figs. 10 to 15, inclusive. Comparison of Figs. 7, 10, 11, and 12 shows that recrystallization starts between 500° and 600°C. and is complete at 700°C., some grain growth taking place at the latter temperature. The grain-size data given in Table 3 show a normal relationship to the annealing temperature with the knee of the curve falling between 1000° and 1100°C. The grain size increases slowly with increasing temperature from 700° to 1000°C. (Figs. 13 and 14) and then

Metal rapidly cooled from the annealing temperature might be expected to show a discontinuity in the curve for temperature versus grain size in the region of this transition but slow cooling apparently masks such an effect; that is, the grain size obtained here is a function not only of the annealing, but also the cooling from the annealing temperature.

The effect of the alpha to beta transformation on physical properties was not studied because of the difficulty of quenching tensile specimens after vacuum heat-treatment. However, the microstructures of titanium rapidly cooled from the annealing temperatures were studied. Specimens rapidly cooled from 800°C. and below showed the normal polyhedral structures; those heated to higher temperatures invariably exhibited an acicular type of

structure differing markedly from that of the furnace-cooled material. Fig. 16 is representative of such structures. It is a typical martensitic structure

graphic planes, thus giving rise to the needlelike pattern not unlike that exhibited by other metals and alloys undergoing similar changes. Diffraction patterns of this

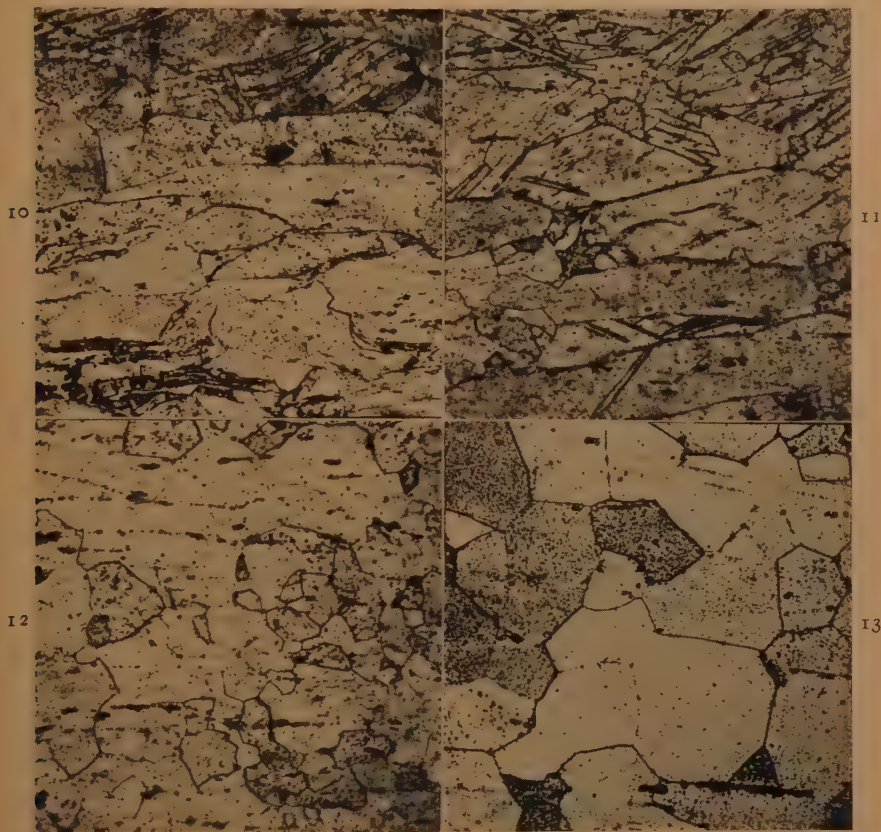


FIG. 10.—COLD-ROLLED TITANIUM ANNEALED 2 HR. AT 500°C.

FIG. 11.—COLD-ROLLED TITANIUM ANNEALED 2 HR. AT 600°C.

FIG. 12.—COLD-ROLLED TITANIUM ANNEALED 2 HR. AT 700°C.

FIG. 13.—COLD-ROLLED TITANIUM ANNEALED 2 HR. AT 900°C. SLOWLY COOLED.

All $\times 250$.

apparently formed by the transformation of beta to alpha titanium and is believed to be due to the relatively large density change that takes place. Beta titanium stable above 875°C. has a body-centered cubic lattice with a density of 4.31 while alpha titanium stable at lower temperatures has a hexagonal close-packed lattice with a density of 4.50. Apparently the transformation proceeds along definite crystallo-

structure are identical with those of alpha titanium produced by slow cooling from above the transformation temperature.

HOT-ROLLING

The high hardness level of cold-worked titanium and the restriction in cold-rolling that necessitated small reductions per pass and frequent annealing, raised the question of hot-rolling the metal.



FIG. 14.—COLD-ROLLED TITANIUM ANNEALED 2 HR. AT 1000°C . SLOWLY COOLED. $\times 250$.

FIG. 15.—COLD-ROLLED TITANIUM ANNEALED 2 HR. AT 1100°C . SLOWLY COOLED. $\times 250$.

FIG. 16.—STRUCTURE OF TITANIUM COOLED RAPIDLY AFTER 2 HR. AT 1100°C . $\times 500$

Kroll² has shown that hot-rolling of titanium is possible and has reported that the hardness decreases from 250 Brinell at room temperature to 80 Brinell at 550°C . It is to be expected, on the basis of this hot hardness, that titanium could be given greater reductions per pass at elevated temperatures and that the total reduction between anneals would be considerably larger than in cold-working. A limiting factor of the hot-rolling is the maximum temperature to which the metal can be heated in air without serious oxidation. A few preliminary tests on the effect of heating titanium in air for 5-hr. periods indicated that while green and sintered compacts showed a measurable increase in weight when heated above 400°C ., those given a preliminary working to close the void spaces showed no significant gain as a result of oxidation at temperatures as high as 500°C . Several early experiments on titanium that had been given an initial cold-working and annealing indicated that such material could be readily rolled at 500°C . with larger reductions per pass than on cold-rolling, and that total reduction up to 75 per cent in thickness was possible without reaching abnormal hardness values. After consideration of these factors, a hot-rolling schedule was adopted, and the remainder of the forged and annealed compacts were rolled at 500°C . The compacts were kept at temperature throughout the rolling by returning to the furnace and reheating after each pass through the rolls. Although reductions as high as 40 per cent per pass could be obtained, reductions of about 15 per cent per pass, 0.037 in. for the initial stage, were made in the normal procedure as compared with 0.004 in. per pass in cold-rolling. The rolling schedule was designed to produce $\frac{1}{16}$ -in. sheet finished with 30, 50, 60, 70, and 80 per cent reduction in thickness by

² W. Kroll: Some Properties of Pure Titanium. *Metallwissenschaft* (1939) 18 (4), 77-80.

hot-rolling. Intermediate annealing to suit the schedule was carried out in a vacuum of 8×10^{-5} mm. Hg or better. All sheet was pickled in 10 per cent HF before annealing, to remove the oxide skin and so prevent its absorption by the metal at the elevated temperature.

TABLE 4.—*Tensile Properties of Hot-worked $\frac{1}{16}$ -inch Titanium Sheet*

Per-centage of Reduction	Ulti-mate Strength, Lb. per Sq. In.	Yield Strength, 0.2 Off-set, Lb. per Sq. In.	Pro-portion-al Limit, Lb. per Sq. In.	Elong-ation, Per Cent in 2 In.	Hard-ness, Rockwell G
0*	74,600	58,600	51,000	22.7	75
30	90,400	82,900	64,700	15.0	82
50	96,900	88,600	69,200	15.1	87
60	100,800	92,300	71,900	12.5	87
70	100,300	90,500	66,700	10.0	88
80	101,700	92,500	68,000	14.8	88

* 60 per cent reduction followed by annealing for 2 hr. at 800°C.

Rolling at 500°C. is not strictly "hot" rolling for titanium, since the micro-structure of material annealed at this temperature exhibits no sign of recrystallization (Fig. 19). If these properties are compared with those of cold-rolled material annealed at 500°C., it will be seen that they are in good general agreement. They cannot be expected to coincide, however, since the amount of reduction differs and total time at temperature also differs; that is, the annealed material was at temperature for 2 hr., while the hot-rolled metal was at the rolling temperature not more than one hour.

The increase of tensile strength for any given amount of hot-rolling is very much less than that produced by the same reduction in cold-rolling. A reduction of 80 per cent by hot-rolling gives a tensile strength of only 101,700 lb. per sq. in. compared with the maximum of 123,000 lb. per sq. in. produced by 50 per cent reduction by cold-rolling. This accords with the relief of work-hardening strains obtained by annealing cold-rolled material at this temperature. It is apparent that work-hardening has taken place, although not to the extent that occurs in room-temperature working. The yield strength shows similar effects increasing to 92,500 lb. per sq. in. for 80 per cent reduction compared with the maximum of 113,500 lb. per sq. in. for 50 per cent reduction by cold-rolling. The percentage of elongation behaves more irregularly but is still about 10 after 70 per cent reduction by hot-rolling, compared with 7.8 for 50 per cent cold-rolling. The value of the elongation at 80 per cent reduction does not fit in with the rest of the data and was not considered in drawing the elongation curve of Fig. 17. Rockwell hardness values increase slowly from an initial G-75 to G-88 after 80 per cent reduction; that is, 4 points below hardness reached by 50 per cent cold-rolling.

Sheet for the study of the effect of annealing temperature on the properties of hot-worked material was finished with 60 per cent reduction and then annealed at temperatures ranging from 500° to 1200°C. The results of such tests are given in

TABLE 5.—*Tensile Properties of Hot-worked and Annealed $\frac{1}{16}$ -inch Titanium Sheet*

Annealing temperature, Deg. C.	Ultimate Strength, Lb. per Sq. In.	Yield Strength, 0.2 Offset, Lb. per Sq. In.	Proportional Limit, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Hardness, Rockwell G	Grain Size, Mm.
500	92,000	84,100	69,000	17.6	81	
600	78,700	63,200	56,300	18.9	75	0.010
700	73,900	59,800	53,400	25.2	74	0.025
800	73,500	59,600	55,100	26.2	74	0.035
900	73,300	59,700	53,400	25.4	76	0.035
1000	80,300	64,800	43,200	22.4	65	0.120
1100	79,500	66,700	45,900	20.2	67	0.120
1200	83,000	67,800	44,600	21.1	70	0.150

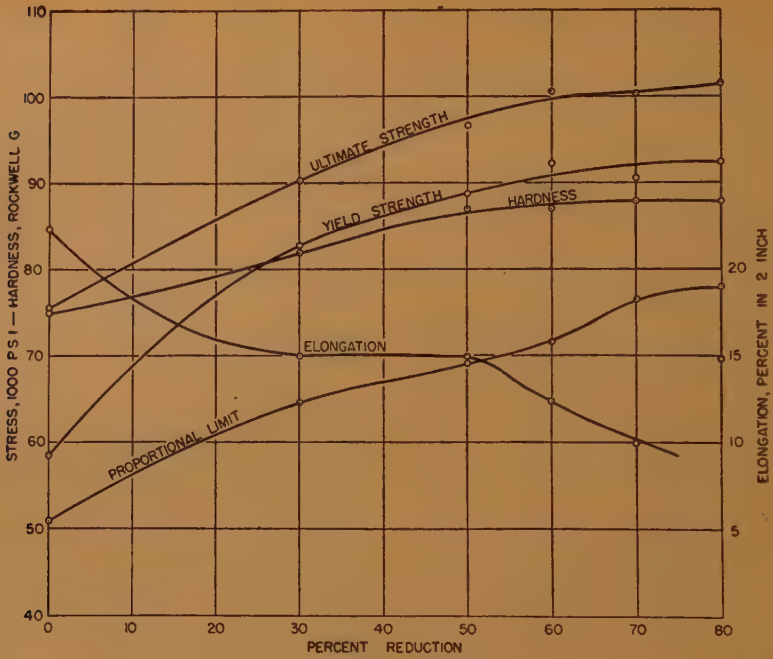


FIG. 17.—PHYSICAL PROPERTIES OF HOT-ROLLED TITANIUM.

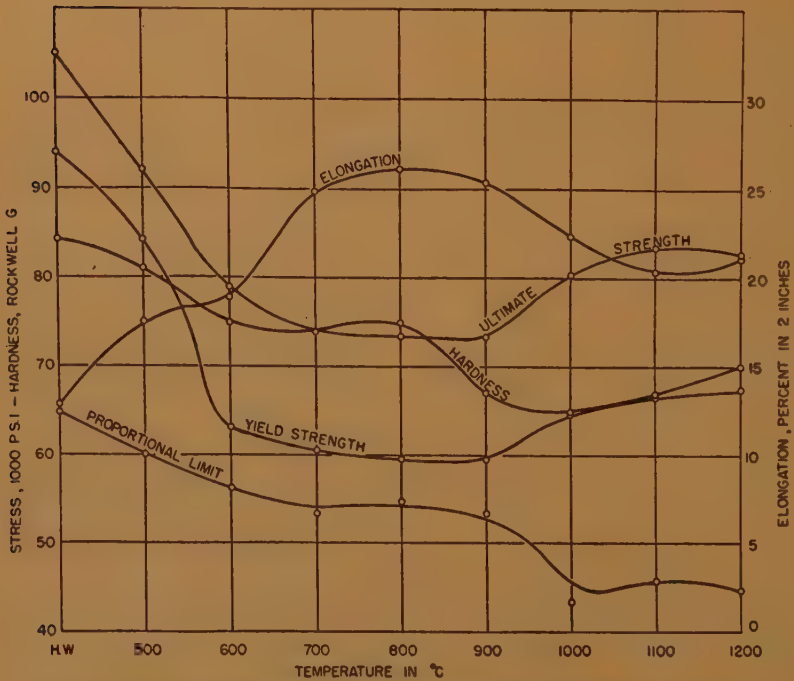


FIG. 18.—PHYSICAL PROPERTIES OF HOT-WORKED AND ANNEALED TITANIUM.

Table 5 and Fig. 18. In general, the properties are similar to those of cold-worked metal annealed at the same temperature. Strength and hardness reach a minimum

corresponding cold-rolled annealed metal up to annealing temperatures of 900°C . but increases with higher annealing temperature instead of remaining constant.

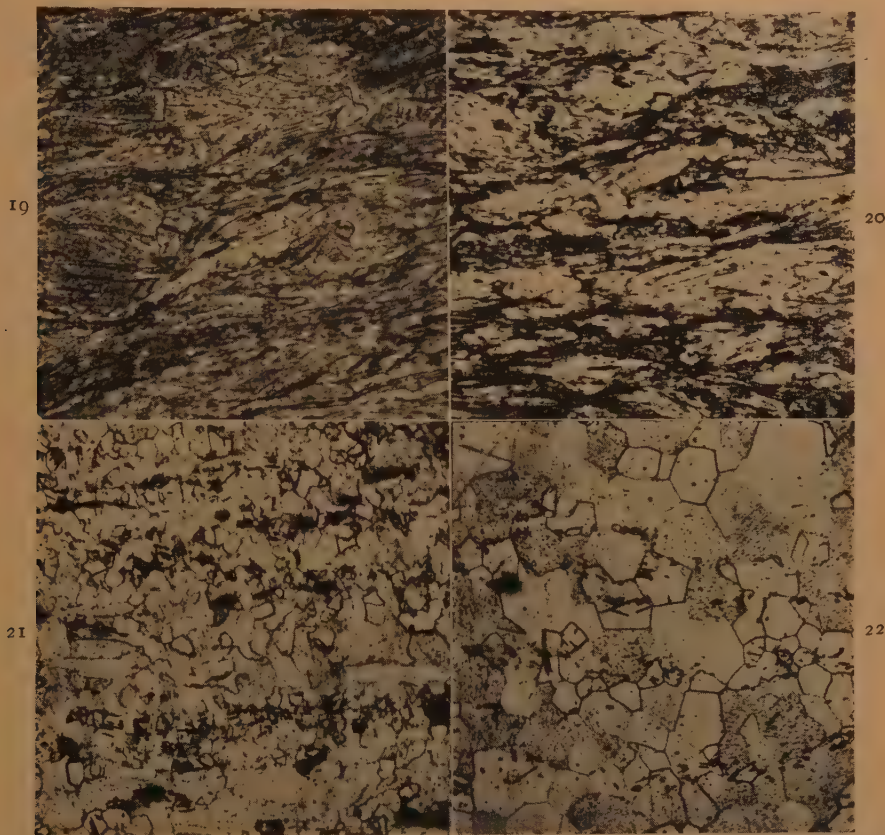


FIG. 19.—STRUCTURE OF TITANIUM "HOT"-ROLLED TO 60 PER CENT REDUCTION IN THICKNESS AT 500°C .

FIG. 20.—HOT-ROLLED TITANIUM ANNEALED 2 HR. AT 500°C .

FIG. 21.—HOT-ROLLED TITANIUM ANNEALED 2 HR. AT 600°C .

FIG. 22.—HOT-ROLLED TITANIUM ANNEALED 2 HR. AT 700°C .

All $\times 250$.

and the elongation a maximum for annealing temperatures of 700° to 900°C . The tensile strength of 73,000 lb. per sq. in. is somewhat lower than that obtained in annealed cold-rolled material. At annealing temperatures of 1000° and 1100°C . the strength increases to the same limiting values in both materials. The yield strength is 3000 to 6000 lb. per sq. in. less than the

The elongation values, while slightly lower up to 700°C . annealing temperature, reach a higher maximum (26 per cent) at 800°C . and remain above that of the cold-worked and annealed sheet for 900° and 1000°C . annealing temperature.

The microstructures of hot-rolled and annealed metal are shown in Figs. 19 to 26. They are very similar to the cold-

rolled and annealed structures and show about the same general trends in grain size.

From the viewpoint of ease of reduction, hot-rolling of titanium at 500°C. offers advantages over cold-rolling. Reductions

requirements for rolling. While the material produced by hot-rolling does not reach the high strength levels of cold-rolled metal, the elongation for equivalent reductions is considerably higher.

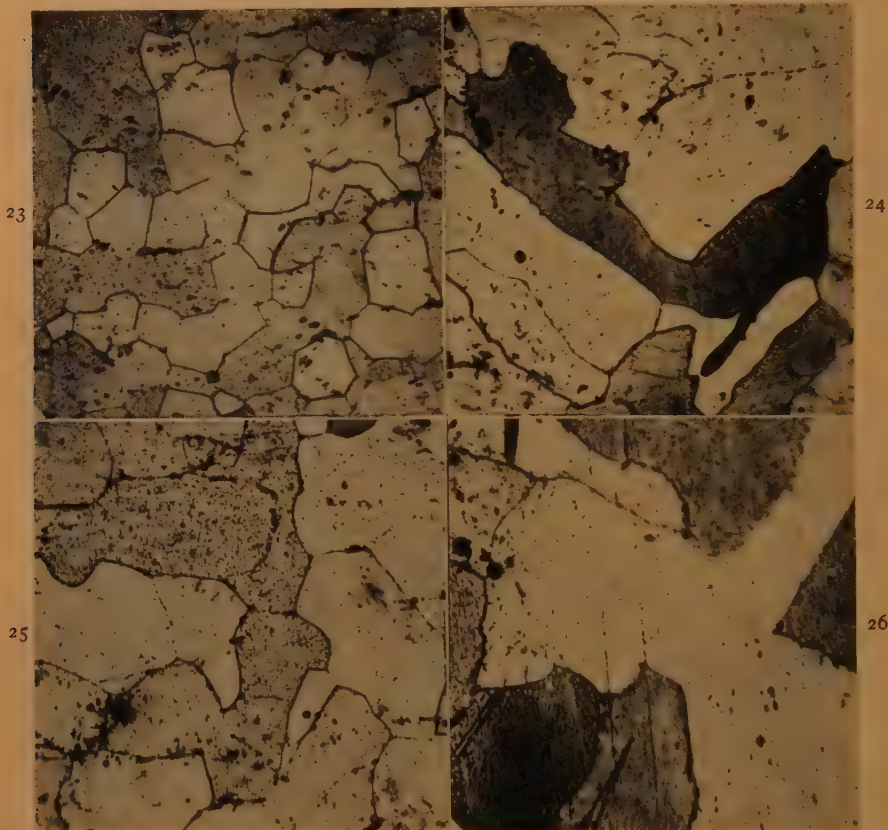


FIG. 23.—HOT-ROLLED TITANIUM ANNEALED 2 HR. AT 900°C. SLOWLY COOLED.

FIG. 24.—HOT-ROLLED TITANIUM ANNEALED 2 HR. AT 1000°C. SLOWLY COOLED.

FIG. 25.—HOT-ROLLED TITANIUM ANNEALED 2 HR. AT 1100°C. SLOWLY COOLED.

FIG. 26.—HOT-ROLLED TITANIUM ANNEALED 2 HR. AT 1200°C. SLOWLY COOLED.

All $\times 250$.

of 80 per cent or more in thickness are quite feasible compared with a maximum of 50 per cent by cold-rolling, and reductions per pass, particularly in the thicker sections, can be greatly increased. This reduces the number of intermediate annealings necessary in the preparation of thin sheet. The drop in hardness at elevated temperatures also decreases the power

ROD AND WIRE

Rod and wire were made from the $\frac{1}{2}$ by $\frac{1}{2}$ by 6-in. compacts and handled in much the same way as the rectangular compacts, except that they were reduced by cold swaging and drawing rather than rolling. The initial reductions amounted to 20 per cent but subsequent reductions were successfully increased to as much

as 50 per cent. In general, the metal appeared to be even more amenable to swaging than to cold-rolling, permitting reductions of 20 per cent in a single die; possibly because the action in swaging is more like that of hammering and gives deeper penetration of the working effect than is obtained by rolling.

Rod less than 0.1 in. in diameter and wire were annealed by heating in air for 20 min. to 1 hr. at a temperature of 600°C. The oxide film formed was very thin and did not penetrate into the metal, since this temperature is low and the time short. Air annealing avoided the time-consuming vacuum anneal and the oxide film was a decided advantage in preventing metal from sticking to the dies. Apparently the oxide film acts as a die lubricant since rod and wire could be easily drawn through 3 dies if it had an oxide coating although vacuum-annealed material could be put through one die only.

The electrical resistivity of annealed wire checks the published value of 56×10^{-6} ohms per centimeter cube and this was not changed significantly by cold-working. Wire as fine as 0.006 in. could be drawn, although it had 15 intermediate air annealings without removal of the oxide film. This suggests that after the first few working stages, with their intermediate vacuum annealing to reduce the void spaces, titanium metal can be handled to advantage by short-time air anneals at 600°C. without harm to the metal by excessive oxidation.

SUMMARY

Titanium metal consolidated from coarse powder has been pressed into compacts at a pressure of 50 tons per square inch, sintered for 16 hr. at 1000°C. in a vacuum of 5×10^{-4} mm. Hg and finished into $\frac{1}{16}$ -in. sheet by a sequence of forging, cold-rolling, and "hot"-rolling procedures.

The sintered compacts have a density of 4.30 and a tensile strength of 83,000 lb. per sq. in., with an elongation of 10 per cent and a hardness of Rockwell G-54. They are best worked by cold forging and may be reduced as much as 50 per cent in thickness in this operation. Compacts normally were forged to 25 per cent reduction and in this condition have a density of 4.42, a tensile strength of 115,000 lb. per sq. in., 6 per cent elongation, and a hardness of G-81. Vacuum annealing for 6 hr. at 1000°C. gives a slight increase in density and reduces the strength and hardness to about those of the sintered compact. These forged and annealed compacts were cold-rolled by slight reductions and many passes, with intermediate annealing after 15 to 20 per cent reduction, and finished into sheet with 10 to 60 per cent reduction.

Tensile strength is increased by cold-rolling from 78,700 to 123,000 lb. per sq. in. by 50 per cent reduction and then drops to 111,500 lb. per sq. in. at 60 per cent reduction, indicating overwork. Percentage of elongation decreases from 25.2 to 8.2 at 20 per cent reduction and drops to 1.5 at 60 per cent reduction. The hardness rises regularly with working from G-76 for annealed material to G-92 for 60 per cent cold-work.

Rolling at 500°C. permits greater reductions per pass and larger total reductions between anneals. The temperature is below the recrystallization temperature of titanium, and material so rolled work-hardens, but to a much smaller extent than in cold-rolling. Reductions of 80 per cent raise the tensile strength to 101,700 lb. per sq. in. and the hardness to G-88, while the elongation drops irregularly to 10 per cent in 2 inches.

Annealing after cold-rolling and hot-rolling produces similar properties for a given annealing temperature. Minimum

strength is reached on annealing between 700° and 900°C. Cold-rolled and annealed metal has a slightly higher tensile strength, 79,000 lb. per sq. in. compared with 73,000 lb. per sq. in., and a hardness of G-79 versus G-75, while the elongation of 25.2 is slightly lower. Annealing temperatures of 1000° to 1200°C. produce a small increase

in the tensile strength and a decrease in elongation.

Some of the metal was swaged into rods and then drawn into wire 0.006 in. in diameter. The small rod and wire could be annealed for further drawing by heating for 20 min. to 1 hr. at 600°C. in air without excessive oxidation.

Silver-thallium Antifriction Alloys

BY F. R. HENSEL,* MEMBER A.I.M.E.

(Fall Meeting, October 1945)

PURE silver and silver-lead alloys have been studied as to their suitability for bearings.¹⁻⁸ A review of the properties of thallium and the silver-thallium constitutional diagram was made by the author to analyze the possibilities of silver-thallium compositions for antifriction materials.† The silver-rich end of the diagram as reported in the literature⁹⁻¹¹ was found to be sketchy and it was necessary to carry out considerable experimental work to arrive at definite conclusions. Some of the results of this work are reported in this paper.

TEST MATERIALS

In the beginning of the work, only fused alloys were investigated. Later, research

TABLE I.—*Composition of Fused Silver-thallium Alloys Tested for Antifriction Properties*

ALLOY No.	PERCENTAGE OF THALLIUM	
1533.....	0.48	} Balance Silver
1534.....	1.06	
231 HT.....	2.04	
231.....	2.10	
232 HT.....	3.83	
232.....	4.07	
233 HT.....	5.86	
233.....	6.38	
234.....	9.84	
234 HT.....	10.07	

was carried out on electroplating methods and diffusion processes. In preparing the fused alloys, care was taken to exhaust the

toxic fumes caused by the thallium content. The compositions of the series of fused alloys are listed in Table I.

The silver-thallium alloys were melted in clay-graphite crucibles and cast into preheated steel molds of $\frac{3}{4}$ -in. diameter. In the cast condition, they showed a cored structure, as indicated by the micrographs of Figs. 1 to 3. The etching reagent used was a mixture of 2 grams $K_2Cr_2O_7$, 8 c.c. H_2SO_4 , and 100 c.c. H_2O .

The cored structure is unsatisfactory for the type of corrosion resistance required for bearing applications, and homogenizing experiments were carried out at various temperatures, the results of which are shown in Figs. 4 through 8. The alloys with a lower thallium concentration, which were heated for 2 hr. at 525°C. show an almost completely homogenized solid solution type of structure.

With higher thallium concentration, the homogenizing temperature was dropped to 475°C. to eliminate the formation of a liquid phase. It is evident that heating for 2 hr. at this temperature did not result in complete elimination of the cored structure.

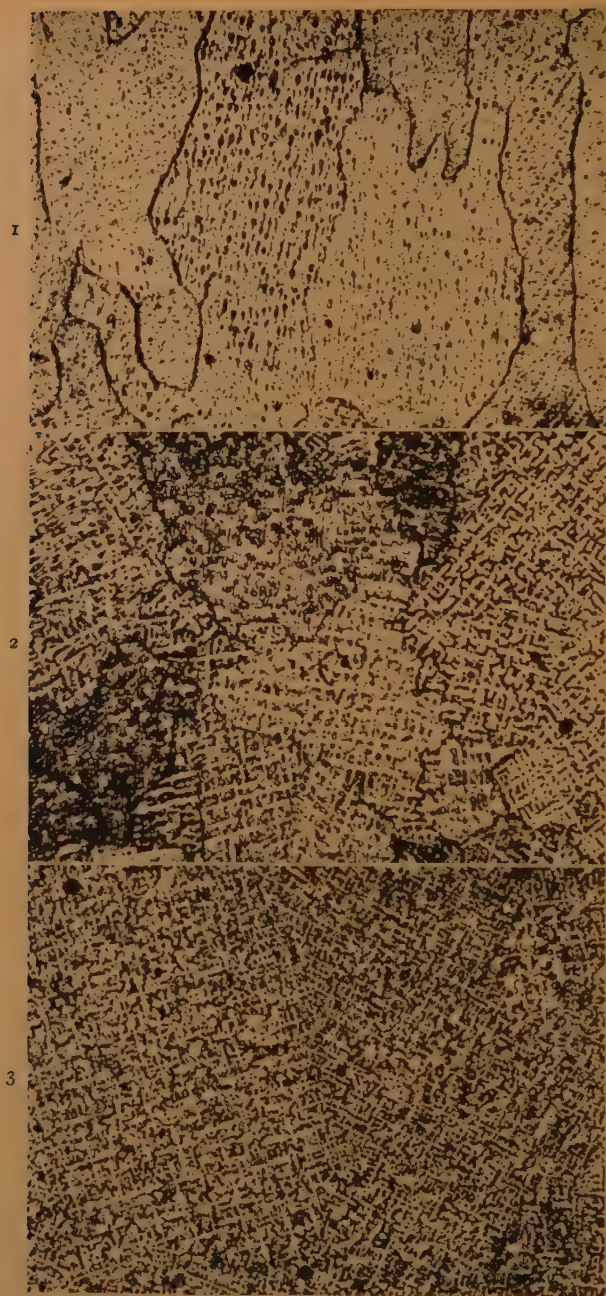
As would be expected, cold-working of the cast structure is an expedient in establishing equilibrium conditions. The fine homogeneous grain structure shown in Fig. 7 corresponds to the cold-worked area under the Rockwell ball penetration when the hardness was taken *before* heat-treatment. A detailed structural study was made on a cast silver-thallium alloy containing 3.67 per cent thallium. Three micrographs (Figs. 9, 10 and 11) show the transition

Manuscript received at the office of the Institute Jan 2, 1945. Issued as T.P. 1930 in METALS TECHNOLOGY, October 1945.

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† Silver-thallium alloys for bearings are covered by U. S. Patent 2375224, issued to F. R. Hensel in May 1945.

¹ References are at the end of the paper.



FIGS. 1-3.—SILVER-THALLIUM CASTINGS. $\times 75$.

Fig. 1. Contains 2.04 per cent Tl.

Fig. 2. Contains 5.86 per cent Tl.

Fig. 3. Contains 10.07 per cent Tl.

from a severely cored structure to a partially homogenized structure after heating for 2 hr. at 400°C. and finally to a complete

The steep drop in electrical conductivity indicates the formation of silver-thallium solid solutions up to about 9 to 10 per cent



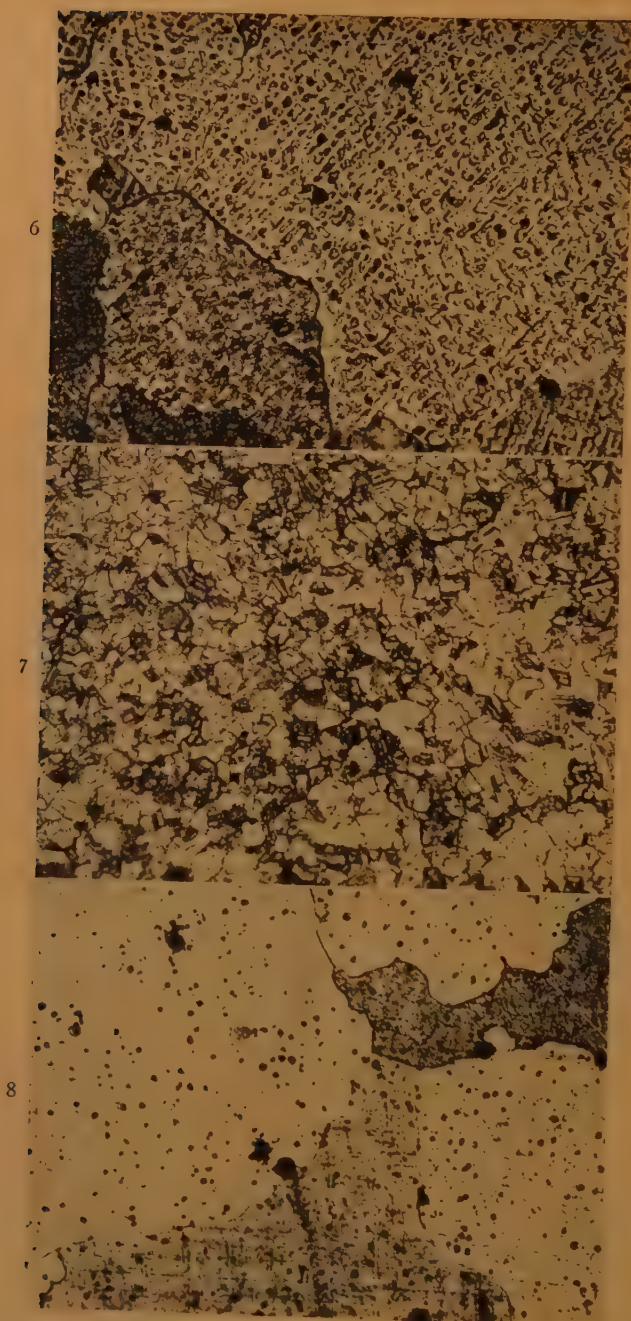
FIGS. 4 AND 5.—SILVER-THALLIUM CASTINGS CONTAINING 2.04 PER CENT Tl. $\times 75$.
Fig. 4. Heated for 2 hours at 400°C.
Fig. 5. Heated for 2 hours at 525°C.

solid solution after heating for 2 hr. at 525°C.

The effect of increasing percentages of thallium on the electrical and physical properties of cast and homogenized alloys is shown in Fig. 12 (electrical conductivity), Fig. 13 (ultimate tensile strength), Fig. 14 (elongation and reduction of area), and Fig. 15 (hardness). Standard A.S.T.M. tensile test bars were used, which were machined from $\frac{3}{4}$ -in. diameter billets cast into preheated steel molds.

thallium, at which percentage the conductivity curves flatten out. This is in agreement with the microscopical data.

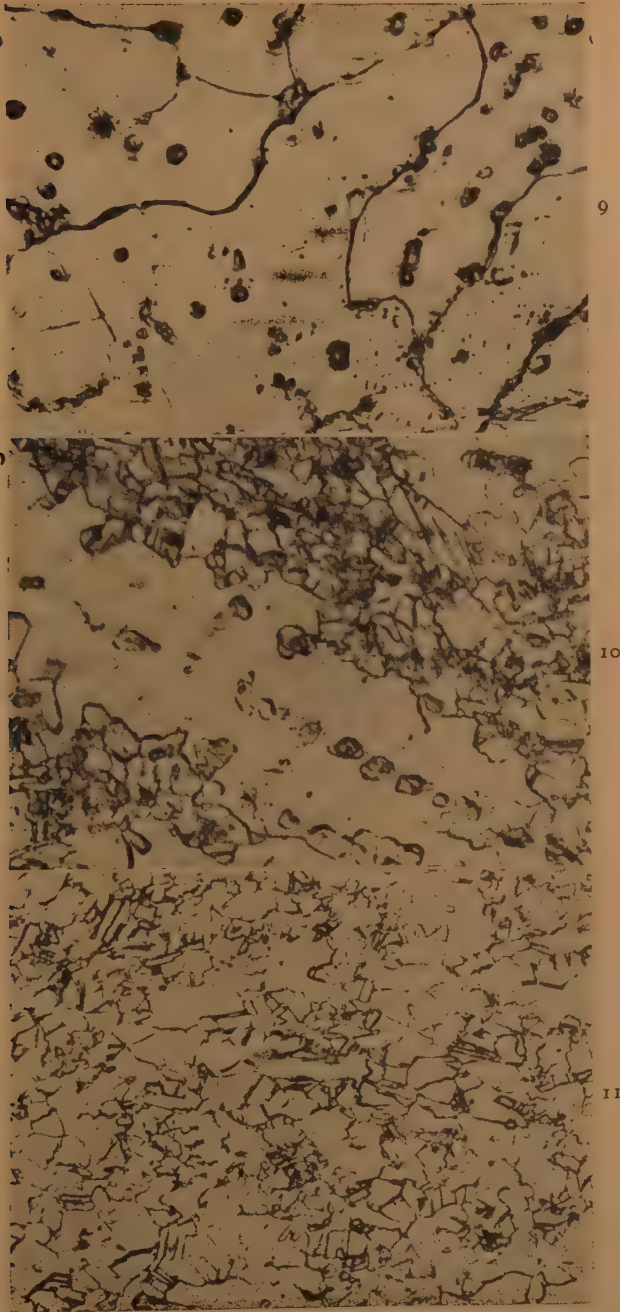
Tensile strength, elongation and reduction of area drop with increasing thallium content, the values in the homogenized condition being higher in almost all specimens than in those in the as-cast condition. The hardness, on the other hand, shows a somewhat erratic behavior, particularly in the alloys of lower thallium contents.



FIGS. 6 AND 7.—SILVER-THALLIUM CASTINGS CONTAINING 5.86 PER CENT Tl. $\times 75$.
 Fig. 6. Heated for 2 hours at 475°C .

Fig. 7. Cold-worked and subsequently heated for 2 hours at 475°C .

FIG. 8.—SILVER-THALLIUM CASTING CONTAINING 10.07 PER CENT Tl. $\times 75$.
 Heated for 2 hours at 475°C .



FIGS. 9-11.—SILVER-THALLIUM CASTINGS CONTAINING 3.67 PER CENT Tl. $\times 250$.

Fig. 9. Untreated.

Fig. 10. Heated for 2 hours at 400°C .

Fig. 11. Heated for 2 hours at 525°C .

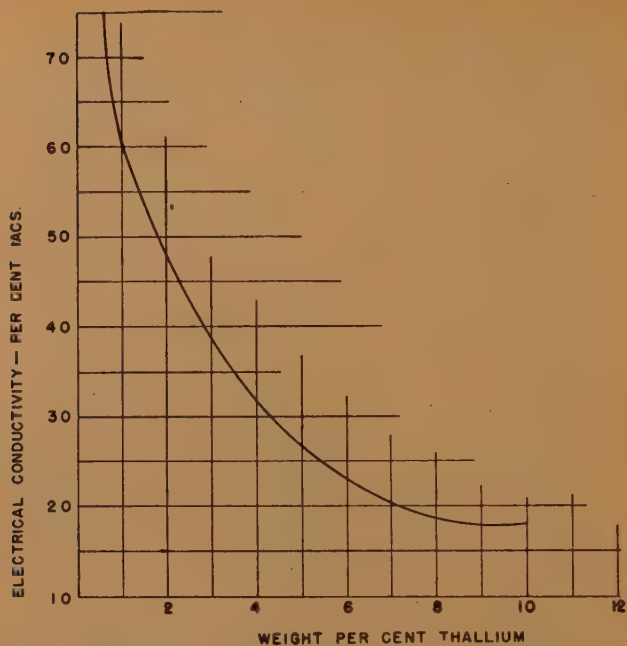


FIG. 12.—ELECTRICAL CONDUCTIVITY, CAST SILVER-THALLIUM ALLOYS.

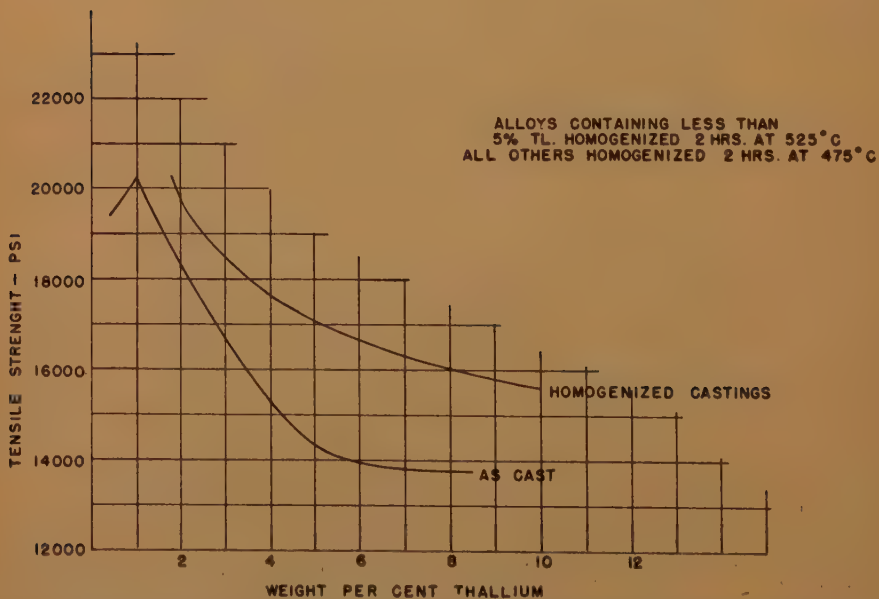


FIG. 13.—ULTIMATE TENSILE STRENGTH OF CAST AND HOMOGENIZED SILVER-THALLIUM ALLOYS.

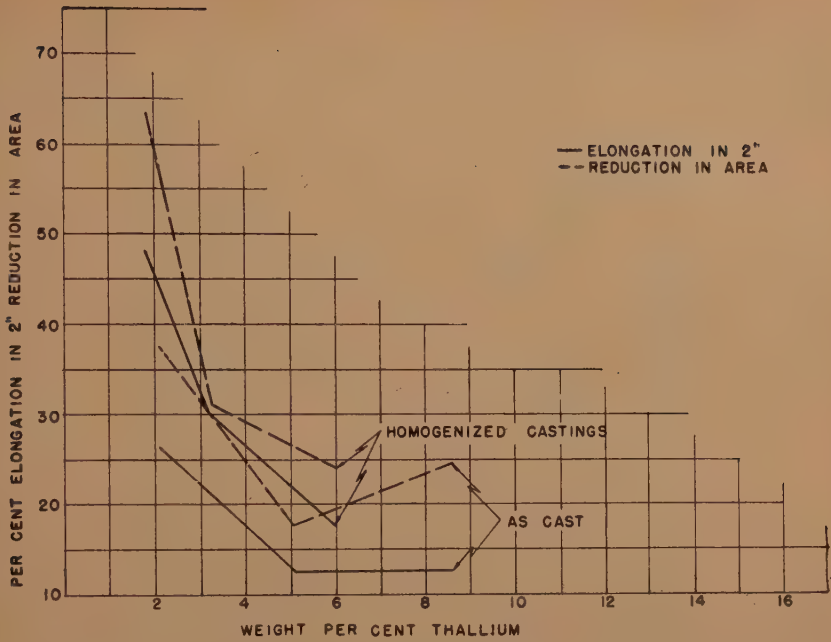


FIG. 14.—PERCENTAGE OF ELONGATION AND REDUCTION IN AREA OF CAST AND HOMOGENIZED SILVER-THALLIUM ALLOYS.

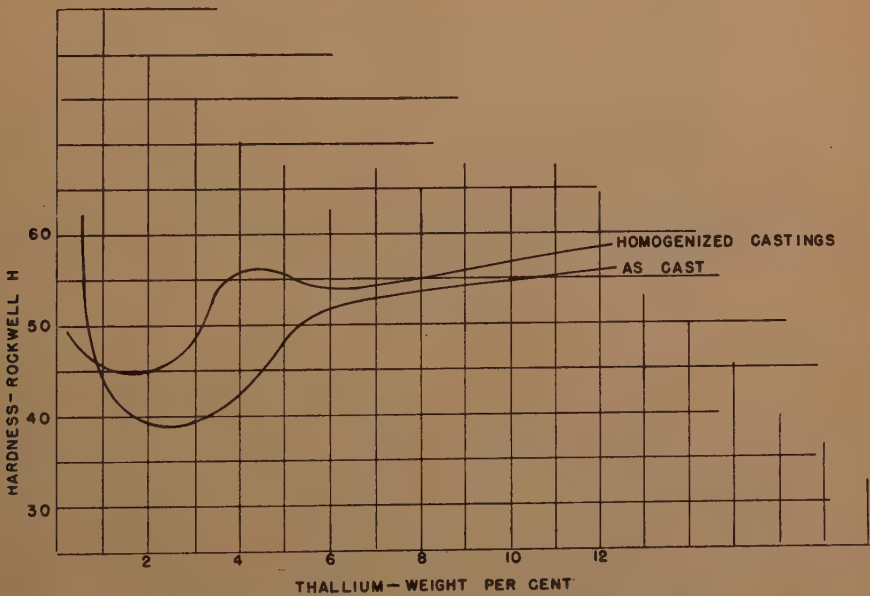


FIG. 15.—HARDNESS OF CAST SILVER-THALLIUM ALLOYS.

SILVER-THALLIUM ALLOYS PRODUCED BY ELECTROPLATING

Alloys were prepared ranging in thallium content from a few hundredths per cent up

silver-thallium anodes containing approximately 2 per cent thallium could be used with a normal silver-plating bath containing no added thallium. If this bath was



FIGS. 16 AND 17.—ELECTROPLATED SILVER-THALLIUM ALLOYS CONTAINING 1.8 PER CENT THALLIUM.
X 500.

Fig. 16. Untreated.

Fig. 17. After homogenizing for 2 hours at 525°C.

to 11.35 per cent. The general character of the deposits at low current densities was coherent and rather smooth. At higher current densities, the character of the deposit was not coherent, and was quite rough and nodular.

In a plating solution containing silver and thallium, selective deposition occurs, the thallium being plated at a much faster rate than the silver. It was found that

operated at current densities of 3 to 8 amp. per square foot, an alloy deposit containing about 2 per cent thallium was obtained after aging of the plating bath. Actual composition of a suitable bath before plating was started was approximately as follows, in grams per liter: silver cyanide, 35; potassium cyanide, 19; potassium carbonate, 38; thalious cyanide, 0.5.

Satisfactory results were also obtained by using a bath in which thalious perchlorate was used in an amount to give an equivalent weight of thallium as thalious

1. As-plated condition: tensile strength, 47,690 lb. per sq. in.; elongation in $\frac{1}{4}$ in., 25 per cent.

2. Homogenized for $1\frac{3}{4}$ hr. at 500°C ..

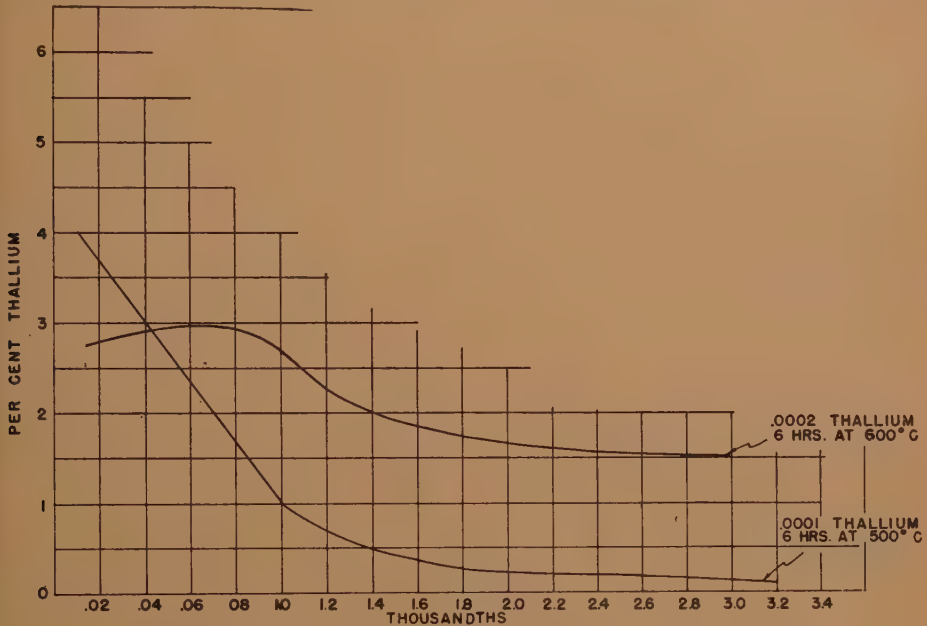


FIG. 18.—FILMS OF THALLIUM ON SILVER DIFFUSED AT 500° AND 600°C .

ion in the solution. A typical bath composition, which was used successfully, was, in grams per liter: silver cyanide, 60; potassium cyanide, 75; potassium carbonate, 38; thalious perchlorate, 13. With this type of bath it was possible to electrodeposit silver-thallium alloys containing approximately 5 per cent thallium.

It was found that the physical properties of the deposit were affected by the current density. The plate produced at high current densities is harder and more brittle, and shows larger crystals, than when the current density is kept low. A maximum current density that would produce suitable deposits was found to be 5 amp. per square foot.

The physical properties of plated strips of the silver-thallium alloy containing 2.12 per cent thallium were as follows:

tensile strength, 29,400 lb. per sq. in.; elongation in $\frac{1}{4}$ in., 46 per cent.

The electrical conductivity of plated deposits was determined as 53 per cent I.A.C.S. on an alloy containing 1.3 per cent thallium, and 45 per cent I.A.C.S. on an alloy containing 1.8 per cent thallium.

MICROSCOPICAL AND X-RAY DIFFRACTION ANALYSIS OF ELECTRODEPOSITED SILVER-THALLIUM ALLOYS

The microscopical structure of a 1.8 per cent thallium-silver alloy is shown in Fig. 16. The fine-grained area with random crystal orientation is adjacent to the steel onto which the alloy was plated. From this zone larger crystals grow. It was noticed in the electroplating of actual bearing shells that the crystal size reached considerable proportions, such as 0.25-in. diameter. A

homogenizing treatment of 2 hr. at 525°C. caused complete recrystallization, resulting in the heavily twinned grain structure seen in Fig. 17.

Further X-ray studies showed that the crystals can rotate around the preferred axis. It appears that the crystals begin to grow from the plating bath in the form of

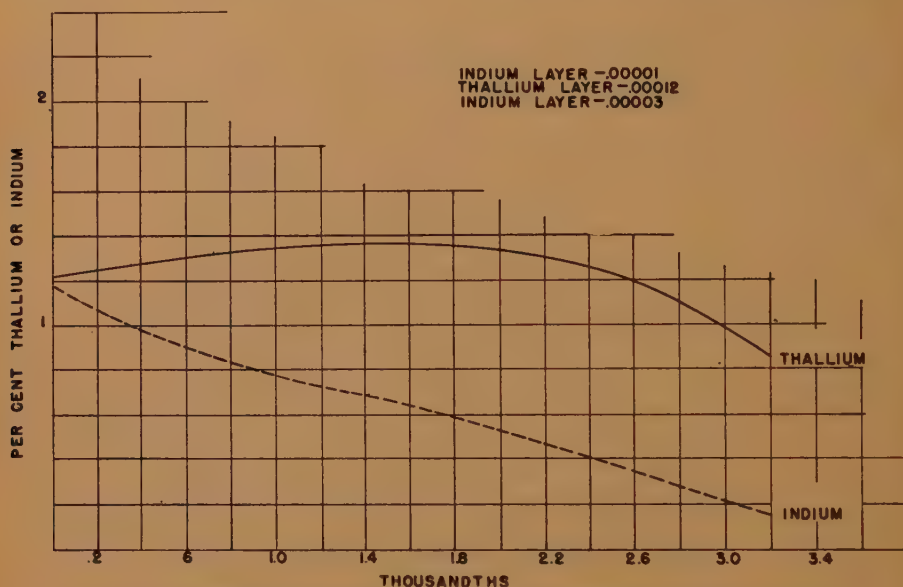


FIG. 19.—INDIUM-THALLIUM-INDIUM ON SILVER, DIFFUSED 6 HOURS AT 600°C.

The X-ray back reflection pictures of the electroplated fine-grained and large-grained zones showed two broad, fuzzy, concentric circles. The lack of sharpness of the diffraction lines may be due either to internal stresses or to a lack of chemical homogeneity, or to both. The back reflection picture after homogenizing showed two sharply defined sets of doublets, indicating a homogeneous and stress-free material. The spottiness of the doublets indicated that grain growth took place during the homogenizing treatment.

The large macroscopical crystals found in bearing shells of electroplated silver-thallium alloys (2 per cent thallium) were studied for evidence of preferred orientation. Back-reflection pictures were taken of single crystals and these showed that predominantly the (100) planes were perpendicular to the direction of the growth of the crystals from the plating solution.

octahedrons, thereby duplicating closely the crystallization phenomena of cubic metal crystals from a molten condition.

A powder-camera picture of a 2 per cent thallium silver alloy in the plated condition revealed the absence of free thallium or a thallium phase and indicates a solid solution of thallium in silver, the lattice parameter of which was found to be practically the same as that of fine silver. The lattice constant for fine silver as given in the literature is 4.077 Å. units. The lattice parameter for fine silver as determined experimentally on a G.E. X-ray diffraction unit, using $\text{CuK}\alpha_1$ radiation, was found to be 4.053 Å. The parameter of the silver-thallium alloy measured under the same conditions was 4.058 Å. The agreement between fine silver and silver-thallium alloy is within the limits of experimental error of the equipment.

DIFFUSION OF THALLIUM INTO SILVER

Since this investigation pertained primarily to the development of a new bearing material where the bearing surface alone

diffusion temperature to 600°C. and keeping the time constant, the gradient was flattened out considerably. The results are shown graphically in Figs. 18, 19 and 20.

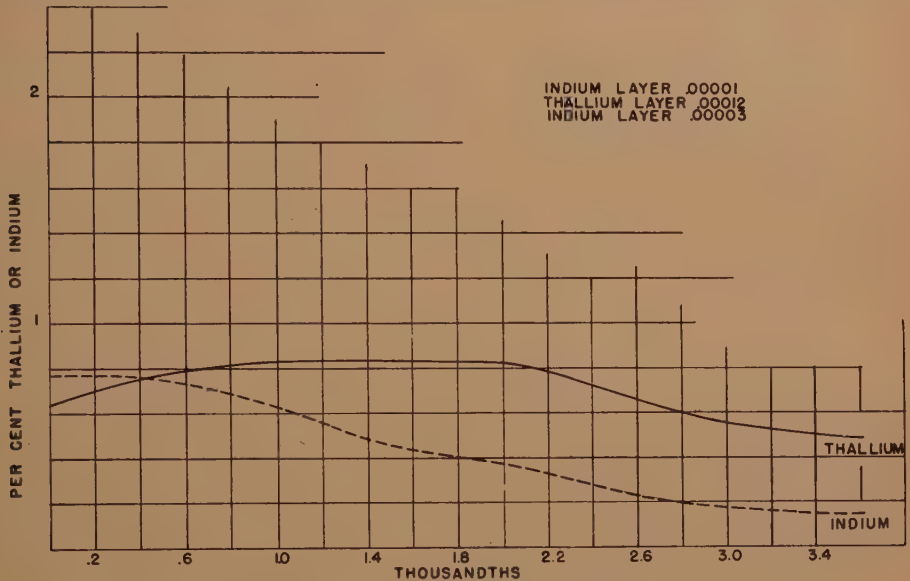


FIG. 20.—INDIUM-THALLIUM-INDIUM ON SILVER, DIFFUSED 12 HOURS AT 600°C.

is of prime importance, the preparation of such surfaces by diffusion was studied. The efforts were directed toward obtaining a uniform silver-thallium alloy having a depth of about 0.002 to 0.003 inch.

The tests were carried out by electroplating a predetermined amount of thallium onto silver and subsequently heating the sample to various temperatures for various lengths of time.

Diffusion experiments were also carried out in which indium and thallium in combination were diffused into the silver. Definite amounts of indium and thallium were electroplated onto the silver, the usual procedure being to first plate indium, then thallium and then indium again over the thallium.

The diffusion gradients are quite steep when diffusion was carried out at 500°C. for 6 hr. in hydrogen, starting the furnace from room temperature. By raising the

BEARING TESTS

Amsler Seizure Tests

The Amsler tests were run on two types of shafts, polished and ground. The tests were conducted as follows: the bearings were first worn in on smooth shafts, then the test shafts were substituted and the tests begun.

Load was applied until the frictional torque reached 4 kg-cm. The load at this point was called, "the Initial Seizure Load." The test continued for one hour, maintaining the torque of 4 kg-cm. centimeters by adjustment of the load. The load at the end of the hour period was called "the Final Seizure Load." The test results are shown in Table 2.

Thallium improves the seizure resistance of silver against a ground shaft, though decreasing it somewhat against a polished

shaft. The alloy containing about 2 per cent thallium appears to be the best.

The silver-thallium alloys are somewhat more seizure-resistant when heat-treated than as cast. The plated thallium-silver alloy exhibits promising properties. The highest final seizure loads on a ground shaft were 55 kg. for the silver alloy containing

A. F. Underwood. Tests were run both in oil whose oxidation to corrosive substances was catalyzed by iron naphthanate and in oil in which the corrodent was oleic acid. The results are shown in Table 3. It was found that the high lead-silver alloy and the copper-lead alloys were corroded but that the thallium-silver alloys were resist-

TABLE 2.—Test Results, Seizure Loads

Specimen No.	Composition, Per Cent				Condition	Seizure Load, Kg.				Ratio of Seizure Load on Ground Shaft to That on Polished	
	Ag	Pb	Tl	In		Polished Shaft ²		Ground Shaft ¹		Initial	Final
						Initial	Final	Initial	Final		
Silver.....	99+				As cast	146	200	30	40	0.21	0.20
A.....	96.53	3.34			As cast	+200	+200	29	37	0.14	0.18
B.....	89.18	10.68			As cast	177	+200	21	33	0.12	0.16
1533.....	99.52		0.48		As cast	+200	+200	29	48	0.14	0.24
1534.....	98.94		1.06		As cast	+200	+200	27	38	0.13	0.19
231.....	97.90		2.10		As cast	117	162	35	55	0.30	0.34
232.....	95.93		4.07		As cast	130	168	29	36	0.22	0.21
233.....	93.62		6.38		As cast	123	183	29	41	0.24	0.22
234.....	90.16		9.84		As cast	132	169	13 ³	39	0.23	0.23
235.....	95.45		3.52	1.03	As cast	134	178	33	43	0.25	0.24
1533.....	99.52		0.48		Anneal 2 hr. 525°C.	+200	+200	28	64	0.14	0.32
1534.....	98.94		1.06		Anneal 2 hr. 525°C.	+200	+200	36	53	0.18	0.26
231 HT....	97.96		2.04		Anneal 2 hr. 525°C.	133	173	45	56	0.34	0.32
232 HT....	96.17		3.83		Anneal 2 hr. 525°C.	132	186	33	39	0.25	0.21
233 HT....	94.14		5.86		Anneal 2 hr. 475°C.	148	+200	34	44	0.23	0.22
234 HT....	89.93		10.07		Anneal 2 hr. 475°C.	135	193	25	36	0.18	0.19
235 HT....	96.03		2.84	0.99	Anneal 2 hr. 525°C.	128	171	35	39	0.27	0.23
Plated Ag Tl.	98		2		As plated	+200	+200	25	57	0.13	0.28
Plated Ag Pb	96.5	3.5			As plated	+200	+200	24	38	0.12	0.19
Plated Fine Ag.....	99.9				As plated	+200	+200	25	36	0.13	0.18

2.10 per cent thallium and 57 kg. for the plated silver thallium. The plated silver lead in this test did not show up better than pure silver. For comparison, the final seizure loads on ground shafts are given for two copper-lead alloys. A material containing 73 per cent copper, 1.05 per cent silver and 25.40 per cent lead showed a final seizure load of 39 kg. An alloy containing 70.67 per cent copper, 26.79 per cent lead, 2.35 per cent tin, showed a final seizure load of 36 kilograms.

Corrosion Tests

A number of corrosion tests were run under standard conditions as prescribed by

ant to corrosion. In only one test of the heat-treated 6 per cent thallium alloy was there appreciable corrosion.

General Motors Tests

The test material was a steel-backed silver-thallium alloy containing approximately 1.8 per cent thallium. The silver-thallium alloy was fused directly to the steel and rolled and formed into half shells.

The size of the test bearings was as follows:

Inside diameter, 2.0 ± 0.0002 inches

Outside diameter, 2.365 ± 0.0002 inches

Length, 1.28 ± 0.005 inches

The test consisted of 48 hr. of operation at a speed of 2500 r.p.m., a load of 2930 lb. per sq. in. and a bearing temperature of 300°F. Oil was fed to the bearings at a pressure of 35 lb. per sq. in. The test proper was preceded by a break-in period of 2 hr. at 1700 r.p.m., 1350 lb. per sq. in. and 3 hr. at 2100 r.p.m., 2060 lb. per sq. inch.

No fatigue failure of the bond was observed. Comparative tests were run with pure silver. The pure silver was rather

the erratic seizing tendency of pure silver may be the cause of the difficulties that have been experienced with it. If this belief is correct, the silver-thallium alloys should perform better in service than pure silver

SUMMARY

1. The microstructure and physical properties of cast silver-thallium alloys containing up to 10 per cent thallium were investigated. In order to obtain materials

TABLE 3.—*Results of Corrosion Tests*

Specimen No.	Analysis, Percentage of Elements						Condition	Wt. Loss of Corrosion, Grams	
	Cu	Ag	Pb	Sn	Tl	In		In Oil Plus Iron Napthanate	In Oil Plus Oleic Acid
Silver.....	?	?					As cast		
A.....		96.53	3.34				As cast	0.000	0.000
B.....		89.18	10.68				As cast	0.002	0.003
C.....	73.43	1.05	25.40				As cast	0.014	0.017
D.....	70.67		26.79	2.35			As cast	0.009	0.012
231.....		97.90			2.10		As cast	0.000	0.000
232.....		95.93			4.07		As cast	0.001	0.000
233.....		93.62			6.38		As cast	0.001	0.000
234.....		90.16			9.84		As cast	0.001	0.000
235.....		95.45			3.52	1.03	As cast	0.001	0.000
231 HT.....		97.96			2.04		Anneal 2 hr. 575°C.	0.001	0.000
232 HT.....		96.17			3.83		Anneal 2 hr. 575°C.	0.000	0.000
233 HT.....		94.14			5.86		Anneal 2 hr. 475°C.	0.004	0.000
234 HT.....		89.93			10.07		Anneal 2 hr. 475°C.	0.001	0.000
235 HT.....		96.03			2.84	0.99	Anneal 2 hr. 575°C.	0.000	0.000

heavily filmed, presumably by a sulphide film, though in other respects the bearings were in excellent condition, apparently being scratched only slightly. The thallium-silver bearings were but slightly tarnished, though they appeared to be more heavily scratched than the silver bearings. However, when the film was removed from the small portion of a silver and silver-thallium bearing, by the mild abrasive action of a pencil eraser, it was seen that there were as many large and deep scratches in one bearing as in the other. The observations on filming may be indicative of differences in the performances of the two bearing materials. Bearing tests indicated in Amsler seizure tests that when there is enough sulphur in the lubricant to cause silver to tarnish, the seizure load is greatly decreased. It is, furthermore, possible that

of true solid solution type, homogenizing treatments at 450° to 550°C. must be applied.

2. Silver-thallium alloys can be obtained by electroplating from cyanide or perchlorate solutions. Homogenizing treatments of electroplated alloys eliminate internal stresses, preferred orientation and non-uniform grain size.

3. The diffusion of electroplated thallium into silver is improved by indium. Alloy layers containing 2 to 3 per cent thallium, of a depth of 0.003 in., are produced by carrying out the diffusion process at 600°C. for 6 to 12 hr. in hydrogen.

4. Amsler seizure tests indicate that a 2 per cent silver-thallium alloy has optimum antifriction properties.

5. The Underwood corrosion test has established extremely low rates of corrosion

of silver-thallium alloys as compared with silver-lead or copper-lead alloys.

6. Silver-thallium alloys containing about 2 per cent thallium passed the General Motors bearing test without any signs of distress.

ACKNOWLEDGMENTS

The author expresses his thanks to Mr. J. W. Wiggs, for his help in the investigation of fused alloys; to Dr. A. R. Ferguson and Mr. J. M. Booe, for the work on electroplating and diffusion; and to Dr. R. W. Dayton, of Battelle Memorial Institute, for his work on the testing of the bearings.

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DISCUSSION

(P. A. Beck presiding)

J. K. ANTHONY.*—I believe that the author's conclusions are sound, i.e., the silver-thallium alloys possess very low corrosion

rates; however, the data in Table 3 do not bring this out nearly as strongly as could be hoped. The losses reported for alloys C and D are not nearly as high as are generally obtained in this procedure. I should like to hear a little more about the exact conditions of the test in order to analyze more thoroughly the data presented.

F. R. HENSEL (author's reply).—The standard Underwood test was used. Unfortunately, nobody in the bearing industry agrees on corrosion tests. The Shell Oil Co. and other oil companies have devised a number of corrosion tests and further work along these lines is under consideration by the author.

P. A. Beck.*—I think that Mr. Anthony's remarks concern the low amount of corrosion, particularly in the oleic acid containing oil with ordinary copper-lead bearings. Such figures as 17 and 12 mg. as are given here for the corrosion of copper-lead bearings in the Underwood test are considered practically zero; for instance, by the Lubrizol Company, which makes most of these tests for the automotive industry. It considers corrosion tests of copper lead bad if the weight loss amounts to about 200 mg. or more. Under normal test conditions, and with an oil containing oleic acid instead of inhibitors, strong corrosion would have been expected.

I have just one more question to ask of Dr. Hensel. Since the Amsler seizure tests and, in fact, all seizure tests, tend to be somewhat erratic, I wonder what the scatter of these data were? There are single figures given in the paper for each alloy in each condition, and I wonder whether the scatter in these tests has been determined. Assuming the usual amount of scatter, the question might be asked whether or not there was any considerable difference between the various alloys with respect to wear. Since the General Motors fatigue test and the Underwood corrosion test failed to show any improvement of the silver-thallium alloy bearings over plain silver bearings, I would ask Dr. Hensel whether there were any actual performance tests in engines that might show, in the field, that the silver-thallium alloy bearings are better than silver bearings.

* Cleveland Graphite Bronze Co., Cleveland, Ohio.

* Cleveland Graphite Bronze Co., Cleveland, Ohio.

F. R. HENSEL.—In the General Motors tests, the surface area of the actual bearing was reduced in order to obtain heavier bearing loads and to simulate an application halfway between an automotive application and an aircraft application. The fatigue properties of silver thallium were found to be excellent. The bearings have not yet been tested in engines.

P. A. BECK.—Silver usually is not considered lacking in fatigue resistance.

F. R. HENSEL.—I agree that silver is an excellent bearing material from the standpoint of fatigue resistance.

J. PALSULICH.*—In the homogenizing experiments on cast silver-thallium alloys, a fine grain structure was obtained (Fig. 7) by cold-working and subsequent heating for 2 hr. at 475°C. It is interesting to note that a similar treatment of a pure silver bearing will result in a definite enlargement of grain size.

Fig. 12 shows the effect of increasing percentages of thallium on the electrical conductivity of the cast alloy. Are these data for the alloy in the as-cast or homogenized condition? Is the information on the conductivity of the electroplated alloy given for the heat-treated condition?

A comparison of the plated versus the cast alloy indicates some interesting information. With 2.12 per cent thallium content, the as-plated alloy has a tensile strength 2.6 times that of the as-cast alloy while the heat-treated plated alloy has a tensile strength of 1.5 times that of the heat-treated cast alloy. The elongation is approximately the same and the electrical conductivity is slightly lower for the plated alloy. Curves for the plated alloys would be very useful, since it is probable that most bearings users would favor the plated as against the cast alloy.

Has the author been successful in achieving a satisfactory bond between the plated alloy and steel? How does this bond compare with that of silver plated on a steel back? On a production basis, how closely can the thallium content of the plated alloy be controlled?

It is interesting to note that the maximum current density that can be used successfully

to plate silver thallium is 5 amp. per sq. ft. This is relatively low compared with pure silver, wherein current densities of 30 amp. per sq. ft. are regularly used.

The diffusion of thallium into silver, shown in Figs. 18, 19 and 20, indicates a positive gradient for a portion of the curves. Does the author have an explanation for this occurrence?

The Amsler test-rig data are interesting but their practical value would have been enhanced considerably if the capacity of the test equipment had permitted the tests to be run to seizure on the polished shaft. The test on the ground shaft, however, does indicate a definite superiority of the plated silver-thallium alloy over the plated silver-lead and plated fine silver. It would be of interest to show the seizure loads on these alloys in the heat-treated state, since both silver and silver-lead have higher seizure resistance when heat-treated.

The writer's experience has indicated the necessity of evaluating two other characteristics of a material in order to obtain a fair comparison of its bearing properties; namely, its resistance to cavitation erosion and its ability to absorb foreign material in the oil.

L. M. TICHVINSKY.*—It is known that there is a trend to develop new bearing alloys because of a belief that the over-a-century-old babbitts are operating at their potential limits. One such development is presented in Dr. Hensel's interesting paper.

In studying the paper it is noted that only very thin layers, 0.003 in. and lower, of load-carrying silver-thallium alloy were investigated. In practice, heavy-duty bearings that operate under high cyclic pressures, such as 3000 lb. per sq. in., have a lining 0.008 to 0.020 in. thick. Experience showed that this range, or the average of 0.014 in., of lining thickness is desirable because of journal roughness and of the size of foreign nonmetallic (dirt) and metallic (weld splatters) particles, which, if trapped in the bearing clearance, should be completely embedded in the lining. Obviously, a very thin layer of bearing alloy will not comply with this important requirement of embeddability.

It would be of interest also to obtain fatigue data by repeated pounding of the silver-

* Wright Aeronautical Corporation, Paterson, New Jersey.

* American Bearing Corp., St. Louis,

thallium alloy of various thickness and compare them with similar data for white bearing alloys, such as tin and lead-base babbitts, alkali-hardened lead, arsenical lead and cadmium-base alloys.

It is believed that uniform nomenclature should be maintained and the hardness of the bearing alloy presented in Brinell numbers instead of Rockwell H scale, as shown on the graph, Fig. 15.

Since approved Underwood corrosion tests may be made for various duration, it is recommended to present final results as rates of corrosion, grams per hour or grams per hour per square inch of bearing area. At what temperatures were the Underwood tests made?

It is known that high localized temperatures may be produced by wiping during semifluid lubrication; therefore, engine designers should know the melting points of bearing alloys, such as the values of solidus and liquidus given for various babbitts. It will be of interest to tabulate the melting points of the silver-thallium alloys for the range 0.48 to 10.07 per cent Tl, as used in the author's experiments.

Continued study of this promising new alloy should be made, especially in connection with prolonged heavy-duty field testing. The latter will yield results that will form the final criterion of technological merits of the silver-thallium alloy. Other considerations, connected with cost and mass production, will then follow.

F. R. HENSEL.—In reference to Mr. Palsulich's comments, the data on electrical conductivity shown in Fig. 12 refer to alloys in the cast condition. The values for the conductivity

of the plated deposits were determined in the as-plated condition.

The silver-thallium alloy in our experiments was not plated directly onto the steel, but onto a silver-base electrodeposit on steel. The silver-thallium layer was approximately 0.003 in. thick after finish machining. The tri-metal will withstand heating to 500°C. in a reducing atmosphere and the chisel test indicated good bond. The thallium content in the electroplated alloy containing 2 per cent Tl is controlled to ± 0.5 per cent of thallium.

The suggestions to determine the seizure loads of heat-treated electroplated silver-thallium alloys, as well as resistance to cavitation erosion and ability to absorb foreign materials in the alloy, are worthy and further experiments along these lines will be carried out.

Mr. Tichvinsky questions the advisability of using very thin layers of electroplated silver-thallium. As pointed out previously, this thin layer of silver-thallium is deposited on a heavy layer of electroplated silver, which in itself is very satisfactory as a bearing material. The plating techniques developed permit the electrodeposition of heavier deposits for special bearing applications where thin layers would be unsatisfactory.

With regard to the melting points of silver-thallium alloys, reference is made to the silver-thallium constitutional diagram, which gives an approximation of the temperatures at which liquid phases exist. The silver-thallium alloys are characterized by a rather wide separation of the liquidus and solidus curves.

Vicalloy—A Workable Alloy for Permanent Magnets

By E. A. NESBITT*

(Chicago Meeting, February 1946)

THE important permanent-magnet alloys 15 years ago contained carbon and depended upon it for their permanent-magnet properties. In recent years great advances have been made in a number of new alloys substantially free of carbon. These include Remalloy,¹ an alloy of iron, cobalt, and molybdenum, the various iron-nickel-aluminum alloys of the Mishima² type, and the more recent Alnico V³ in which the best properties are developed by heat-treating in a magnetic field. The Mishima and the Alnico types of alloys are very brittle and after casting must be ground to size. This article describes a permanent-magnet material⁴ that can be machined as cast, and when handled with some care can be rolled to thin sheet and drawn to fine wire. Optimum magnetic properties are developed by a simple heat-treatment, and at this time the ductility of the alloy disappears. If the cast alloy is heat-treated without cold-working the magnetic energy product is about 1.0×10^6 . This material is called Vicalloy I (pronounced vicalloy, *V* for vanadium, *I* for iron, and *C* for cobalt). When the alloy is first hot-worked and then considerably reduced in area by cold-swaging, drawing or grooved rolling, it is found that after heat-treatment the magnetic energy product measured in the direction of previous extension can be increased to 2.0 to 3.5×10^6 . These higher values have been

obtained only after reductions in area of 75 to 95 per cent, and since the material hardens considerably during working, the reduction ordinarily can be accomplished only in fine wires, although larger sizes can be reduced by the use of powerful machinery. When the material has been cold-worked in such a manner as to improve its energy product substantially, it is called Vicalloy II.

Commercial use of Vicalloy has been made in the recording of speech. Tape 0.002 by 0.050 in. has been found superior in quality to all others tried, and is now used in the Western Electric Mirrorphone.⁵ In a variety of forms Vicalloy I or II is useful in many laboratory instruments, and in experiments in which the sizes and shapes required cannot be obtained with the other more brittle permanent-magnet materials.

In 1936, during a study of other age-hardening magnetic systems, it occurred to the author that some of the iron-cobalt-vanadium alloys might be suitable for permanent magnets. The proportions of iron, cobalt, and vanadium were varied and a range of alloys of particular interest was found, as shown by the indicated area in Fig. 1. The limits of this range of composition are 30 to 52 per cent iron, 36 to 62 per cent cobalt, and 4 to 16 per cent vanadium. The compositions indicated by points outside this area were also tested.

PREPARATION AND PROPERTIES OF VICALLOY I

The alloys were usually cast in graphite molds into bars $\frac{3}{4}$ in. in diameter and

Manuscript received at the office of the Institute Sept. 4, 1945. Issued as T.P. 1973 in METALS TECHNOLOGY, February 1946.

* Bell Telephone Laboratories, Murray Hill, New Jersey.

¹ References are at the end of the paper.

about 20 in. long. Some of the castings were swaged hot to $\frac{3}{4}$ -in. diameter. By quenching at a high temperature and aging at a lower temperature, the best

In Table 1 are given results of magnetic measurements for this composition on a $\frac{3}{4}$ -in. bar after it had been given several heat-treatments. These heat-treatments

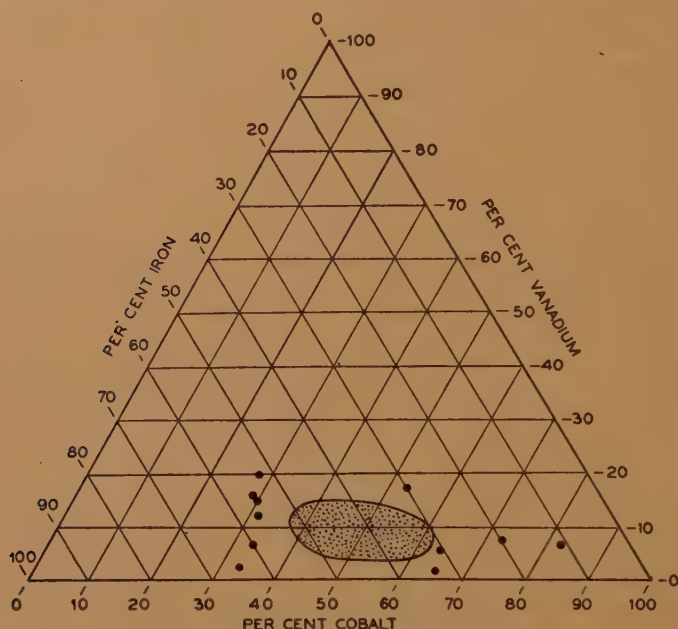


FIG. 1.—COMPOSITIONS TESTED.

Indicated area shows range of composition extensively explored.

permanent-magnet properties were developed in an alloy containing about 38 per

TABLE 1.—*Magnetic Measurements on $\frac{3}{4}$ -inch Bar*

COMPOSITION: 37.2 PER CENT FE, 52.9 CO, 9.4 V, 0.6 SI (BY ANALYSIS)

Heat-treatment	Residual Induction B_r	Coercive Force H_c	Flux Density B for $H = 1735$
As cast in graphite mold.....	5,040	64	16,250
8 hr. at 600°C.....	6,890	295	14,100
20 min. at 1200°C. Quenched in oil.....	4,950	51	18,300
8 hr. at 600°C.....	9,000	300	16,160
1 hr. at 1100°C. Furnace cooled.....	5,270	56	18,650
8 hr. at 600°C.....	8,630	299	15,850

cent iron, 52 per cent cobalt, and 10 per cent vanadium.

were all applied to the same bar in the order listed.

After the best heat-treatment the bar had a residual induction of 9000 gaussess and a coercive force of 300 oersteds with a maximum energy product $(BH)_m$ of 1.0×10^6 . Curves for the corresponding demagnetization and energy products are shown in Fig. 11, curve 3. The values of B_r and H_c for this bar show that an anneal may be substituted for a quench; i.e., the material may be cooled slowly or rapidly from the high temperature. After the quench or anneal, it is necessary to age the bar at 600°C. to obtain the permanent-magnet properties. This is a unique result among permanent-magnet alloys of the age-hardening class in that the first heat-treatment may involve slow cooling, which tends to produce equilibrium conditions.

Because this alloy may be cooled slowly as part of its heat-treatment, pole tips made from soft material (usually slowly cooled) may be welded to the magnet and

within this range. The residual induction decreases slightly with increase in quenching temperature but this is offset by a small increase in coercive force. *The fore-*

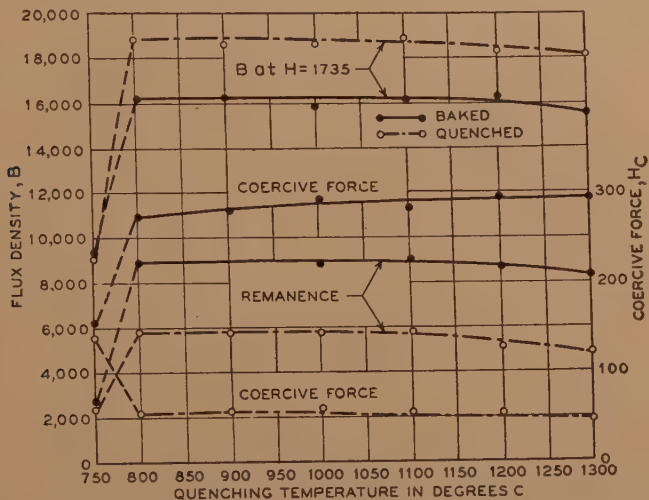


FIG. 2.—VARIATION OF MAGNETIC PROPERTIES WITH QUENCHING TEMPERATURE.

the magnet and pole pieces may be heat-treated together. Thus the usual deleterious effects of welding pole tips to magnet after heat-treatment are avoided.

A $\frac{3}{4}$ -in. bar of the same composition was swaged hot to $\frac{1}{4}$ in., and a series of tests was made to determine the effect of varying the quenching temperatures from 1300° to

going data show that this alloy is exceptional in having a wide range of quenching temperatures, a low minimum quenching temperature, and great flexibility in rate of cooling.

The results cited thus far show that Vicalloy has magnetic properties similar to those of the well-known Honda steel



FIG. 3.—VICALLOY WIRE, $\frac{1}{8}$ -INCH DIAMETER, TWISTED COLD AFTER COLD-WORKING.

750°C. The results are shown in Fig. 2. After quenching, the specimens were held at 600°C. until the best properties were obtained. Fig. 2 shows that there is an optimum temperature range for quenching, extending from 800° to 1300°C., but that 750°C. lies outside this range. The final quality of the material varies only slightly

(36 per cent Co, 4 W, 2 Cr, 0.8 C, 0.3 Mn, bal. Fe) but that its mechanical properties before the final heat-treatment are superior to other alloys of comparable magnetic strength. This is very important because most commercial magnets of good quality must be ground, and cannot be cold-worked. Fig. 3 shows a Vicalloy wire of

$\frac{1}{8}$ -in. diameter that was twisted cold after cold-working. The iron-nickel-copper alloys of Neumann, Buchner and Reinboth⁶ are mechanically soft and also will yield a

effect of cold-working is removed; that is, the magnetic results are about the same as on hot-worked samples. Examples of the effect of cold groove rolling are shown

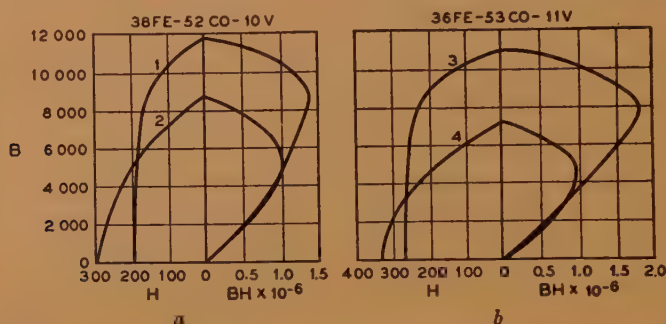


FIG. 4.—COMPARISON BETWEEN SPECIMENS THAT HAVE BEEN DOUBLE HEAT-TREATED (CURVES 2 AND 4) AND SPECIMENS THAT HAVE BEEN COLD-WORKED FOLLOWED BY HOLDING AT 600°C. (CURVES 1 AND 3), SHOWING SUPERIORITY OF LATTER.

maximum energy product of 1.0×10^6 . In order to attain this energy product these alloys are normally quenched, cold-rolled about 75 per cent, and finally aged.

VICALLOY II

In experimenting with a Vicalloy specimen (38 per cent Fe, 52 per cent Co, 10 per cent V) that had been reduced a few per cent by cold-swaging, it was noted that the material had a slightly higher energy product.⁷ This was obtained merely by heat-treating after the working without any intermediate annealing or quenching. By using this same procedure but increasing the degree of cold-working on a given alloy instead of using the double heat-treatment, the residual induction was increased and the coercive force decreased; and the demagnetization curve obtained was so changed in shape that the maximum energy product $(BH)_m$ was materially increased. A fullness factor, $(BH)_m/B_rH_c$, as high as 73 per cent has been measured. The methods of cold-working that produce elongation such as swaging, rolling between grooved rolls, and wire drawing are more effective than flat rolling, which usually permits spreading. If the cold-worked specimens are heated above 800°C. the

effect of cold-working is removed; that is, the magnetic results are about the same as on hot-worked samples. Examples of the effect of cold groove rolling are shown in Fig. 4 for specimens containing 38 per cent iron, 52 per cent cobalt, 10 per cent vanadium, and for those with 36 per cent iron, 53 per cent cobalt, and 11 per cent vanadium. In this figure the curves for demagnetization and energy product are shown for these two compositions for specimens quenched and aged, and for specimens merely aged after a cold reduction of 75 per cent in area of cross section. By the latter method $(BH)_m$ for the 10 per cent vanadium alloy is increased 39 per cent over that obtained with the double heat-treatment. In the alloy containing 11 per cent vanadium the $(BH)_m$ is increased 95 per cent. A further addition of vanadium makes the improvement even greater, as will be shown by later curves. In Table 2 are listed results obtained after cold elongation of a number of Vicalloys ranging from 8 to 14 per cent vanadium. The final treatment was holding for one or more hours at 600°C.

This table shows that the final energy product increases with increase in vanadium up to 14 per cent. The progressive effect of cold elongation on the maximum energy product for the compositions listed in Table 2 is shown by the curves in Fig. 5. In general the rate of increase of $(BH)_m$

with reduction in area becomes greater with increase of vanadium content. Although Vicalloy with 14 per cent vanadium is almost nonmagnetic before it is cold-

tion on the energy product of the 14 per cent vanadium alloy is exhibited in Fig. 7. In Fig. 8 curves are shown for 4 and 14 per cent vanadium alloys, the first showing

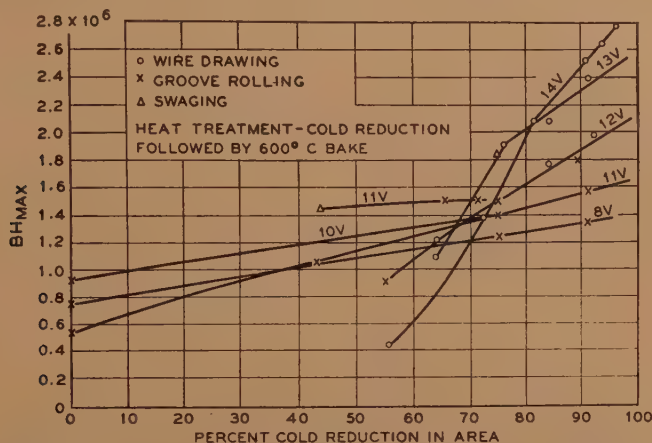


FIG. 5.—VARIATION OF MAXIMUM ENERGY WITH PERCENTAGE OF COLD REDUCTION IN AREA.

worked, this alloy yields an energy product of 2.8×10^6 after a cold reduction in area of 95 per cent and aging at 600°C . for a wire of 0.038-in. diameter. Fig. 6 shows the curves for demagnetization and energy product for successive stages of elongation of the alloy containing 8 per cent vanadium. The exceptionally large residual induction of 14,200 gaussess shown in Fig. 6 occurs with a coercive force of 130 oersteds. The striking effect of cold elonga-

a residual induction of 18,000 gaussess and the second a maximum energy product of 3.56×10^6 . These are the highest values obtained on the Vicalloy series.

DIRECTIONAL PROPERTIES

The magnetic properties just discussed were all measured in the direction in which the specimen was elongated during mechanical working. At right angles to this direction the permanent-magnet properties are

TABLE 2

Attempted Composition			Magnetic Properties ^a					Reduction Diameter in Inches		Reduction in Area, Per Cent
Fe	CO	V	B_r	H_c	$(BH)_m \times 10^{-6}$	B_d	H_d	From	To	
38.5	53.5	8	14200	130	1.35	12000	113	.50	.125	94 ^b
38	52	10	11700	195	1.38	8800	155	.50	.25	75 ^b
38	52	10	11800	190	1.55	9300	165	.330	.160	76 ^d
36	53	11	11400	220	1.58	9200	170	.50	.125	94 ^b
36	53	11	11000	270	1.85	8000	230	.25	.125	75 ^c
35	54	11	9100	315	1.38	6100	225	.75	.470	60 ^b
35	53	12	10500	300	1.98	8000	250	.312	.090	92 ^d
35	57	13	10000	375	2.38	7700	310	.312	.095	91 ^d
34	52	14	9600	400	2.78	8150	340	.187	.038	96 ^d

^a The flux density B_d and the magnetizing force H_d are for the maximum energy product $(BH)_m$, which is the maximum magnetic energy available for external use as in an air gap.

^b Cold groove-rolled.

^c Cold-swaged.

^d Cold-drawn.

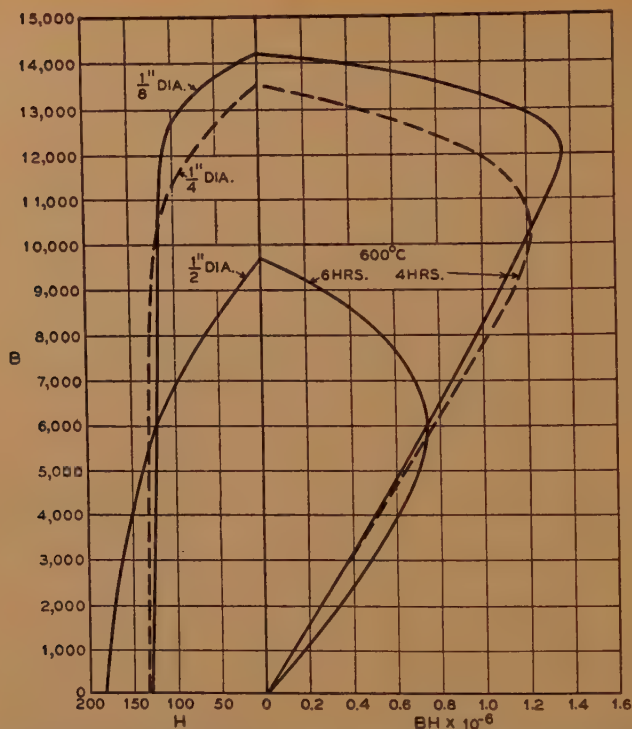


FIG. 6.—EFFECT OF COLD GROOVE ROLLING ON MAGNETIC PROPERTIES OF VICALLOY. Composition: 38.5 per cent Fe, 53.5 Co, 8 V. Bar, $\frac{3}{4}$ -in. dia., was hot-swaged to $\frac{1}{2}$ -in. dia., then reduced cold to $\frac{1}{8}$ -in. dia. Specimens were tested at $\frac{1}{2}$, $\frac{1}{4}$, and $\frac{1}{8}$ inch.

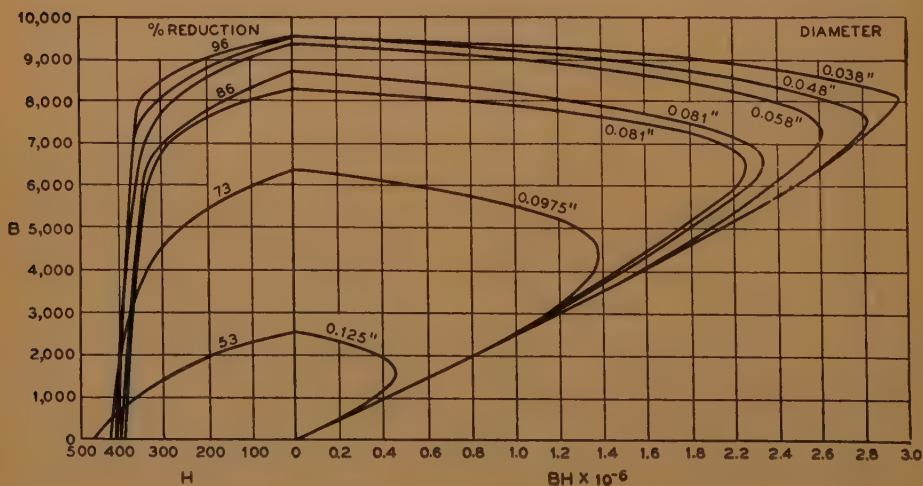


FIG. 7.—EFFECT OF WIRE DRAWING ON VICALLOY. Composition: 34 per cent Fe, 52 Co, 14 V. Cold reductions were followed by holding at 600°C.

inferior. The directional properties of Vicalloy after rolling cold and holding at 600°C . are shown in Fig. 9 for a specimen containing 35 per cent iron, 54 per cent

and then stacked together and again measured longitudinally. This result is shown by curve 2, and the lower values are due to the effect of the air gaps intro-

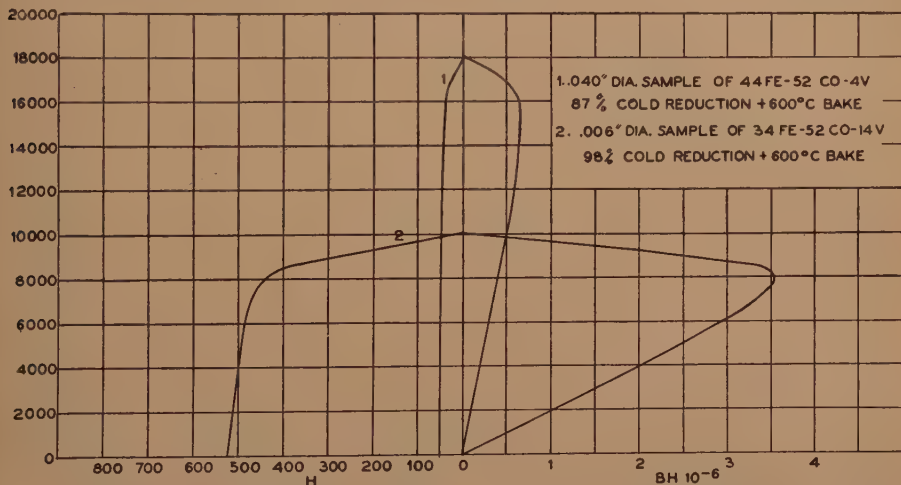


FIG. 8.—HIGHEST VALUE OF RESIDUAL INDUCTION AND ENERGY PRODUCT OBTAINED ON VICALLOY SERIES.

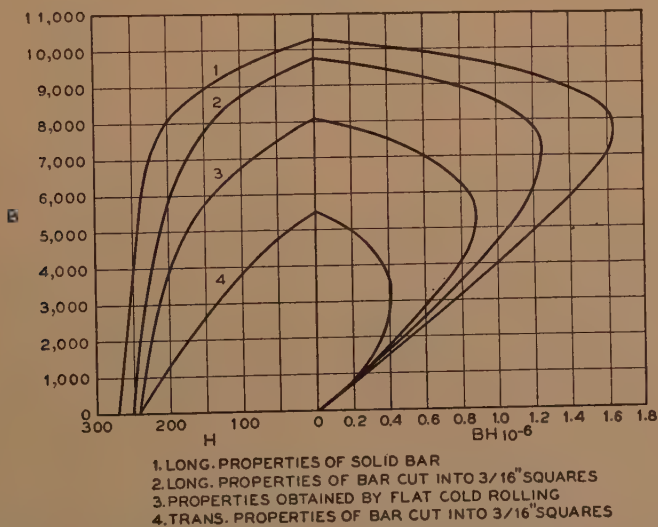


FIG. 9.—DIRECTIONAL MAGNETIC PROPERTIES OF COLD-GROOVE-ROLLED VICALLOY AFTER AGING at 600°C .

cobalt, 11 per cent vanadium. Curve 1 shows the longitudinal properties of a solid bar $\frac{3}{16}$ in. square. After this test was made the bar was cut into $\frac{3}{16}$ -in. cubes

duced. The same pieces were then stacked together so that their properties could be measured in a direction at right angles to the direction of cold elongation. Curve 4

shows the result of this test. The coercive force is about the same in both directions, but the residual induction and energy product are much lower in the transverse

maintain all the high-temperature alpha phase on cooling to room temperature. At room temperature it is then in a super-saturated condition. For best permanent-

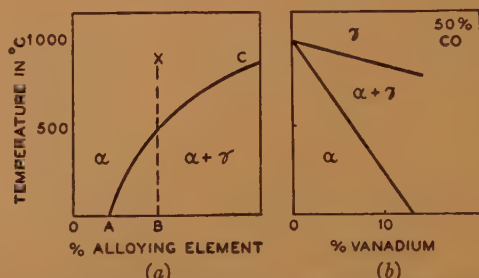


FIG. 10.—COMPARISON OF TYPICAL PHASE DIAGRAM (a) FOR DISPERSION-HARDENING PERMANENT-MAGNET ALLOYS WITH THAT FOR VICALLOY (b).

direction. A contrast of the properties obtained in the longitudinal and transverse directions is shown by the difference between curves 2 and 4.

Measurements on flat cold-rolled material of the same composition are also shown in Fig. 9, curve 3, which lies about halfway between the curves taken in the longitudinal and transverse directions for the $\frac{3}{16}$ -in. square material. Flat cold-rolling that permits spreading produces small directional effect, and does not yield the high energy product produced by the other methods of cold-working. Cold-swaging, cold groove-rolling, and wire drawing produce a much more marked effect on these alloys. In other words, methods of working that cause elongation rather than spreading are most effective.

PHASE STRUCTURE

The behavior of Vicalloy may be better understood by considering the constitutional diagram of the iron-cobalt-vanadium system and contrasting it with the diagrams of some other system such as iron-molybdenum. The latter may be considered typical of an age-hardenable alloy used as a permanent magnet. As shown in Fig. 10a, this alloy of composition X must be quenched from some temperature above the solubility curve AC to

magnet properties, the alloy is raised to an intermediate temperature below the solubility curve and a small quantity of the low-temperature gamma phase precipitates. The alloy then consists of a small amount of the low-temperature phase dispersed in a matrix of the high-temperature phase.

The diagram of Fig. 10b is given by Koster and Lang⁸ for iron-cobalt-vanadium alloys. According to this, when an alloy of 9.5 per cent vanadium is in equilibrium at room temperature, it consists entirely of the low-temperature phase. X-ray photographs taken in these Laboratories of specimens ($\frac{1}{4}$ -in. dia. by 12 in. long) containing 9.5 per cent vanadium showed almost exclusively lines attributable to the low-temperature alpha phase, when the specimens were either quenched (1000°C.) or slowly cooled. High coercive force was produced by raising the temperature of the alloy to the two-phase region (e.g., 600°C.) and holding there for an hour or more, thus permitting a small amount of the high-temperature gamma phase to disperse in a large amount of the low-temperature alpha phase. This situation is thus the reverse of that in the iron-molybdenum system.

When the vanadium content was 11 to 14 per cent vanadium, the alloy upon

cooling to room temperature was found to contain some of the high-temperature phase. After the cold reduction, however, only the low-temperature phase was

other existing permanent-magnet alloys, and this difference can readily be understood in terms of the constitutional diagram of the system.

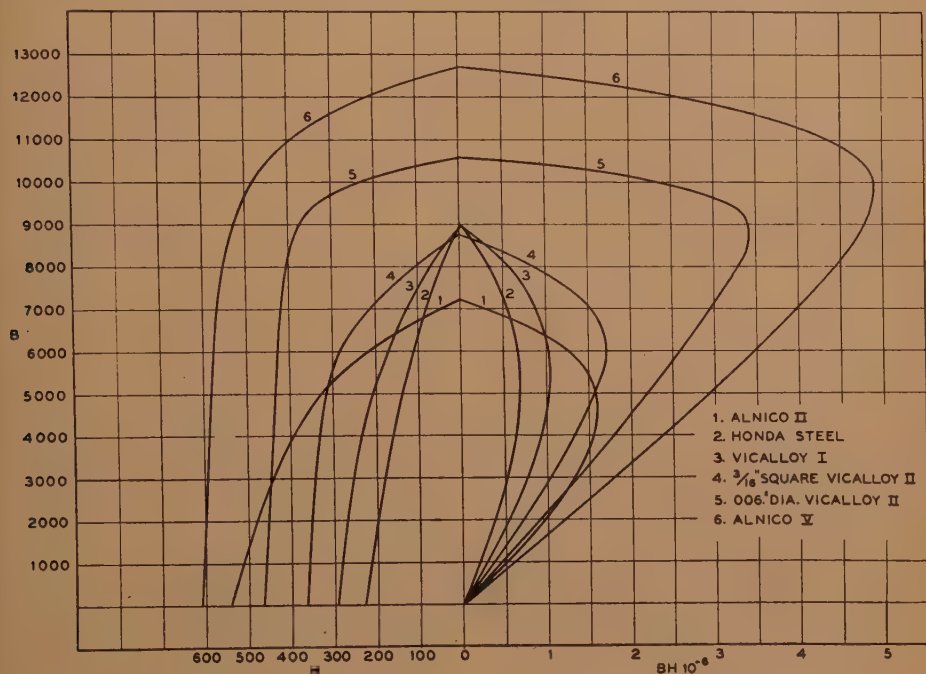


FIG. 11.—COMPARISON OF VICALLOY WITH COMMERCIAL PERMANENT ALLOYS.

present in any considerable proportion. These higher vanadium alloys were then hardened by holding at 600°C. after the cold reduction.

The cold-working has an advantageous effect in all of these alloys in addition to bringing about the phase transformation just mentioned. It appears to produce an orientation of the crystals that increases the residual induction and the maximum energy product in the direction elongated. This effect is easily noticed in Fig. 4, especially Fig. 4*b*, and in Figs. 6 and 7. X-rays confirmed the fact that increasing preferred orientations accompanied increased elongations.

From the foregoing it is evident that Vicalloy is fundamentally different from

PRECAUTIONS IN MELTING AND FABRICATING

Best magnetic properties were obtained on Vicalloy when the interstitial impurities were reduced to a minimum. Small amounts of aluminum are harmful to the final magnetic properties and should be kept under 0.3 per cent. Care should be taken in the selection of the ferrovanadium used to introduce vanadium in the melt, as commercial grades may contain aluminum in undesirable amounts. A small quantity of manganese (0.3 per cent) was usually added to our melts to take care of the free sulphur.

For drastic reductions to small cross sections, such as that of the 0.002 by

0.050-in. tape used in magnetic recording,⁵ great care must be exercised in melting and casting to avoid oxide inclusions, blowholes, cracks and pipes in the ingot. Any such imperfections may be carried on through and cause difficulties in the final reductions in thin tape or fine wire. A horizontal mold has been used successfully to prevent such troubles in small castings. The material for tape is cast in graphite molds, hot-swaged at 1000°C., cold-rolled to size, and heat-treated.

During cold-working the alloys work-harden rapidly. The hardness may rise from 30 to 40 on the Rockwell C scale during a cold reduction of 50 per cent in area. The material has been drawn on a standard commercial bench from 0.33 to 0.16-in. diameter without intermediate anneals. The following data for a specimen of Vicalloy II (37.5 per cent Fe, 52 Co, 10.5 V) shows the variation of hardness for several treatments, which were applied in the order listed:

TREATMENT	ROCKWELL C HARDNESS
30 min. at 1000°C. Quenched in oil.	20
60 per cent reduction in area by cold-swaging.	39
1 hr. at 600°C.	60

COMPARISON WITH OTHER PERMANENT-MAGNET ALLOYS

Fig. 11 gives a comparison between these alloys and commercial permanent magnets. Vicalloy I refers to the 9.5 per cent vanadium alloy, which does not depend on cold-working to raise its energy product. This alloy can be rolled, machined, punched, tapped and drilled. The maximum energy product of the alloy (1.0×10^6) is about the same as that of Honda steel or Remalloy and is inferior to Alnico II. Vicalloy II refers to the 13 per cent vanadium alloy, whose best magnetic properties are obtained by cold elongation plus heat-treatment. This alloy has an energy product of 3.5×10^6 in a 0.006-in. diameter wire and an energy product of 1.74×10^6 in a $\frac{3}{16}$ -in. square section, both

of which are higher than Alnico II. The high energy product is accompanied by a high residual induction and a demagnetization curve of unusual shape, having a relatively high, sharp bend.

The more recent Alnico V has a higher magnetic energy product than any of those mentioned above. This alloy, known abroad as Ticonal, has an energy product of 4.5 to 5×10^6 , attained by heat-treatment in a magnetic field. Although for many purposes this alloy is unsurpassed, it still is limited in application because it is not machinable and must be ground to shape. The usefulness of the Vicalloys rests on their superior combination of magnetic and mechanical properties.

SUMMARY

A new permanent-magnet material has been developed with unusual working as well as magnetic properties. Specimens that have been cast or subjected to a small amount of hot reduction by rolling or swaging may be machined, punched, tapped, or drilled. After being either quenched, annealed, or given the usual cold finishing passes and then heated for 2 hr. at 600°C., such materials have a magnetic energy product of 1.0×10^6 , about the same as Honda steel. The preferred composition for Vicalloy I is 38.5 per cent iron, 52 per cent cobalt, and 9.5 per cent vanadium. Vicalloy II is produced by severe cold reduction of the material after hot-swaging. Following a cold reduction of 75 to 95 per cent and a subsequent simple heat-treatment, the energy product is 2.0 to 3.5×10^6 . The preferred composition for Vicalloy II is 35 per cent iron, 52 per cent cobalt, and 13 per cent vanadium.

ACKNOWLEDGMENTS

The author is greatly indebted to Mr. G. A. Kelsall and Dr. R. M. Bozorth, who aided and encouraged this work, and to

Mr. F. E. Haworth, who made the X-ray measurements. In addition, Mr. D. H. Wenny and Mr. H. T. Reeve contributed to the melting, casting, and fabricating technique of these alloys.

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A Study of the Behavior of Rutheniopalladium in Torch Flames, with the Object of Improving Soldering Technique

By R. H. ATKINSON* AND G. P. GLADIS*

(Chicago Meeting, February 1946)

PALLADIUM has been used for jewelry for many years, particularly in conjunction with gold. This use increased in amount during the war, as palladium and gold were only moderately used for war purposes while demands for platinum and some of the other members of the platinum group were so great that their use in jewelry was prohibited. Palladium hardened with a small percentage of ruthenium has the necessary technical properties and appearance for good jewelry, and it is sufficiently rare to be desirable for luxury items—at least 100 times as rare as gold.

Although both visual and spectrophotometric examination demonstrated that the color of palladium was almost the same as that of platinum, a few jewelers found the surface of palladium, even after some polishing, rather dark in areas that had been repeatedly heated during the soldering necessary to assemble certain types of handmade ornaments. This phenomenon is not to be confused with the thin, bluish oxide film that can be produced by heating in air over the range 400° to 800°C., as that film is easily reduced by dipping in warm 5 per cent formic acid or in warm methanol.

It was suspected that the difficulty arose from heating in atmospheres that were alternately oxidizing and reducing, as

Wise and Vines¹ had found that this opened the grain boundaries of palladium and palladium-silver alloys in the same manner as in pure silver, as reported by Martin and Parker.² This damage is caused by the reaction between oxygen in solid solution in the metal, acquired when heated under oxidizing conditions, and hydrogen diffusing in from subsequent heating under reducing conditions; the steam cannot diffuse out and therefore builds up sufficient pressure to disrupt the metal near the surface. Copper and various other metals can be damaged similarly, but platinum is nearly immune; therefore the problem was new to the platinum jeweler. Sulphur in the fuel gas also can cause trouble but did not appear to be dominant in the present instance.

Metallographic examination of both pure palladium and ruthenium-palladium showed that the usual torch using oxygen and city gas as normally operated did in fact cause the surface and subsurface damage that had been observed, and also disclosed that a reducing flame caused more damage than an oxidizing flame and was very damaging even in the absence of any intentional swing in atmosphere from oxidizing to reducing (Fig. 7); besides the surface damage, there was serious loss of ductility. A full explanation of the mechanism of attack is not evident at the moment, but may be allied to the attack that occurs on heating catalytically active metals in nonequilibrium atmospheres.

¹ References are at the end of the paper.

Manuscript received at the office of the Institute Nov. 10, 1945. Issued as T.P. 1982 in METALS TECHNOLOGY, April 1946.

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A detailed examination of the effect of torches fed with various fuel gases and operated reducing, "neutral" and oxidizing was instituted, which showed that the oxy-

inferior to the oxyacetylene. An oxidizing oxyhydrogen flame was fair, but a reducing oxyhydrogen flame was rather poor. Oxy-city gas, even when oxidizing, was

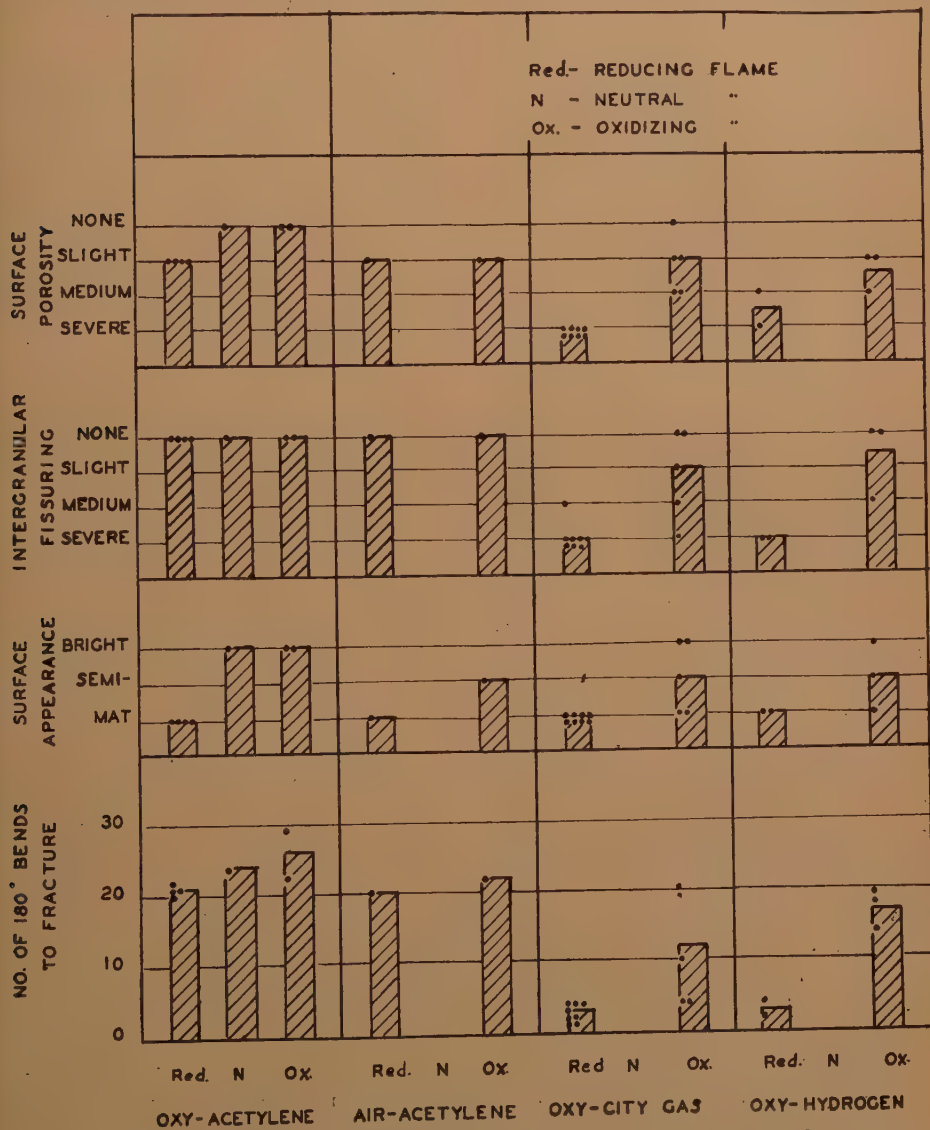


FIG. 1.—EFFECTS OF VARIOUS TORCH FLAMES ON RUTHENIOPALLADIUM.

acetylene flame produced the least damage and was particularly good when operated "neutral" or slightly oxidizing (Fig. 2). Air-acetylene flames were only slightly

inferior to oxyacetylene and was extremely bad when operated under reducing conditions. These relations are summarized in Fig. 1.

Practical plant trials have confirmed the virtues of the neutral or slightly oxidizing oxyacetylene flame for soldering palladium with platinum solders melting as high as 1400°C. In the absence of other facilities, the same type of flame can be used for annealing small parts also. This procedure almost completely eliminates the surface damage that may be expected to occur with flames of other types.

MATERIALS AND EQUIPMENT

A laboratory sample of 4.5 per cent rutheniopalladium (melt No. 1170) was used for most of the tests in which the effects of different torch flames were investigated. This alloy was prepared from commercially pure palladium sponge and ruthenium powder. The pure metals were melted in an induction furnace, in a sand crucible, lined with zircon cement; the alloy was deoxidized with commercial carbon monoxide and cast into a graphite mold of $\frac{3}{8}$ -in. diameter. The small ingot was cold-rolled to strip 0.020 in. thick, with four intermediate anneals in helium at 1100°C. for 30 minutes.

All important results were confirmed with commercial samples of 4.5 per cent rutheniopalladium made by two different refiners; these two samples will be referred to as "commercial A" and "commercial B" in this report. A small, commercial oxyacetylene welding torch with replaceable tips was used because of the need for close control of the temperature and size of flame. Tips with orifices 0.4, 0.9, 1.0, 1.3 and 2.0 mm. in diameter, respectively, were chosen for the various gas mixtures to obtain comparable flame conditions. For instance, with the very hot oxyacetylene torch a small flame was necessary, in order to avoid overheating the samples, whereas with the cooler oxy-city-gas and oxyhydrogen flames, especially if reducing, large flames, necessitating large orifices, were used to raise the samples to the desired temperature. The gas

mixtures selected for the tests were oxy-city gas, borated oxy-city gas, oxyhydrogen, oxy-carbon monoxide, oxyacetylene* and air-acetylene.* Oxy-city gas is the mixture now used by the jewelers in general for their soldering operations and the other gases were examined with the object of finding a gas mixture that would not impair the ductility of palladium heated in it.

Preliminary tests showed that the type of flame employed (i.e., oxidizing, neutral, or reducing) was very important. With oxyacetylene, the reducing—commonly called carburizing—flame is produced by burning an excess of acetylene. It can be recognized by the secondary luminous cone of a distinctly greenish color surrounding the white inner cone and extending into the outer envelope. The neutral flame has a well-defined white inner cone without any greenish tinge of acetylene at its tip. The oxidizing flame has a shorter and more sharply defined inner cone, which is less luminous. With oxy-city gas, oxyhydrogen, and oxy-carbon monoxide the differences between reducing and oxidizing flames are not so clearly defined because only one cone appears within the flame envelope, and it is impossible to recognize a neutral flame by appearance. An excess of oxygen produces a short, sharply defined cone while a deficiency in the supply of oxygen produces a longer and broader inner cone.

TEST METHODS

The test samples, $\frac{1}{2}$ by $\frac{1}{8}$ by 0.020 in., were prepared from cold-rolled 4.5 per cent rutheniopalladium strip that had been annealed in helium at 1100°C. for 30 min and water-quenched. A sample was first given one 90° bend in the vise (see later) and was placed on the bottom of an inverted alundum combustion boat with the bend of the specimen upward. The torch

* The acetylene tank was nearly full, precluding any possibility of interference by solvent acetone, which becomes a factor when a tank is nearly empty.

was clamped in position to direct the flame at the bend of the sample from above at about a 45° angle. The bend was about $\frac{1}{4}$ in. away from the tip of the inner cone for the reducing flame and $\frac{1}{2}$ to 1 in. away from the inner cone of the oxidizing flame and about the same distance from the inner cone of the neutral flame.* The temperature of the flame at the position of the sample was maintained at $1200^\circ\text{C}.$ by checking with a platinum-rhodium-platinum thermocouple. To simulate the conditions of alternate heating and cooling that occur during soldering operations, the sample was heated in the torch flame for 45 sec., and then removed and allowed to cool in air for 45 sec. This cycle was repeated 10 times. At the completion of the 10 cycles the sample was allowed to cool to room temperature before the bend test was begun. Several tests for hot shortness were made by rapidly pressing down on the bend of a sample while it was at $1200^\circ\text{C}.$ at the finish of the 10 cycles. There were also modifications of the regular 10-cycle run, such as water-quenching or cooling in city gas between heating periods instead of cooling in air, and continuous heating for the same total heating time instead of intermittent heating.

After the flame test each sample was clamped in a small vise, provided with jaws rounded to a radius of 0.15 in., and bent by hand backward and forward through an angle of 180° until it broke. The number of bends (180°) was counted.

The broken pieces were freed from superficial palladium oxide film by a short immersion in warm 5 per cent formic acid and the appearance of the surface was assessed: i.e., bright, semimat or mat. The assessments are purely relative, but it was thought worth while to make them because of the importance attached to a good color in a metal used for settings for diamonds. Representative samples were then mounted in lucite for microexamina-

tion of sections at right angles to the heated surfaces; all samples were etched electrolytically in 5 per cent sodium cyanide (5 volts a.c.).

EFFECT OF DIFFERENT TORCH FLAMES ON RUTHENIOPALLADIUM

Results and observations are given in detail in Table 1 and are summarized graphically in Fig. 1. The micrographs of Figs. 2 to 11, to which the results of the bend tests have been appended, summarize the effect of the three principal flames—oxyacetylene, oxy-city gas and oxyhydrogen—on rutheniopalladium.

Oxyacetylene.—Irrespective of the type and size of the flame, oxyacetylene did not affect the ductility of the samples except when the flame was strongly reducing, when it caused a slight loss of ductility (Table 1). All samples heated in oxidizing or neutral oxyacetylene flames remained bright but those heated in the reducing flame became mat. Microexamination revealed that samples heated in neutral or oxidizing flames (Figs. 2 and 4) had not been affected in any way although samples that had been heated in a reducing flame showed some surface deterioration to a depth of 0.5×10^{-3} in., but no intergranular fissures (Figs. 3 and 5).

Air Acetylene was not quite as good as oxyacetylene. Although ductility was well maintained in both oxidizing and reducing flames, there was some loss of brightness accompanied by the formation of slight subsurface porosity.

Oxy-city Gas.—Samples heated in the oxidizing flame remained ductile, had a bright or semimat appearance and were free from porosity or intergranular fissures (Figs. 6 and 8). Samples heated in the reducing flame showed serious loss of ductility and had a mat appearance, and microexamination revealed subsurface microporosity with intergranular fissures to a depth of 3×10^{-3} in. in the laboratory

* Neutral flame only used with oxyacetylene.

TABLE 1.—Effect of Different Torch Flames on Ductility, Microstructure and Brightness of 4.5 Per Cent Rutheniopalladium
 Flame-heating test: 45 seconds in flame; 45 seconds cooling in air; 10 cycles. Temperature of specimen: 1200°C. Ductility test (cold):
 Number of 180° bends (0.15-inch radius) to fracture. Specimen size: $\frac{1}{8}$ by $\frac{1}{8}$ by 0.020 inch

Sample No.	Ruthenio- palladium Melt No.	Gas Mixture	Flame Condition	Diam- eter of Torch Orifice, Mm.	Number of 180° Bends to Fracture	Appear- ance of Metal Surface	Microstructure of Section Perpendicular to Heated Surface
68	1170	Oxyacetylene	Oxidizing	0.4	29	Bright	Good surface; no intergranular fissures
77	1170		Oxidizing	0.4	22	Bright	Good surface; no intergranular fissures
66	1170		Neutral	0.4	24	Bright	Good surface; no intergranular fissures
67	1170		Reducing	0.4	20	Mat	Irregularly deteriorated surface; no intergranular fissures
68	1170		Reducing	0.4	21	Mat	Slightly deteriorated surface; no intergranular fissures
63*	1170		Reducing	0.4	21	Mat	Slight surface porosity; no intergranular fissures
73	Commercial A		Reducing	0.4	22	Mat	Slight surface porosity; no intergranular fissures
70	Commercial B		Oxidizing	0.4	18	Bright	Slight surface porosity; fine voids in grain boundaries
74	Commercial A		Reducing	0.4	19	Bright	Slightly deteriorated surface; fine voids in grain boundaries
75	Commercial B		Reducing	0.4	16	Semimat	Slight surface porosity; fine voids in grain boundaries
108	1170	Air-acetylene	Reducing	0.4	16	Semimat	Deteriorated surface; fine voids in grain boundaries
106	1170		Oxidizing	1.0	22	Mat	Slight surface porosity; no intergranular fissures
84	1170		Reducing	1.0	20	Mat	Good surface; no intergranular fissures
86	1170		Oxidizing	1.0	19	Bright	Narrow surface porosity; no intergranular fissures
69	1170		Oxidizing	1.0	20	Bright	Narrow surface porosity; no intergranular fissures
72	1170		Oxidizing	2.0	10	Mat	Medium surface porosity; very slight intergranular fissuring
88	1170		Oxidizing ^b	1.0	4	Mat	Medium surface porosity; severe intergranular fissuring
85	1170		Reducing	1.3	2	Mat	Deteriorated surface; severe intergranular fissuring
87	1170		Reducing	1.0	4	Mat	Severe surface porosity; severe intergranular fissuring
83	1170		Reducing	2.0	4	Mat	Severe surface porosity; severe intergranular fissuring
89	1170	Oxy-city gas	Reducing	2.0	2	Mat	Severe surface porosity; severe intergranular fissuring
73	1170		Reducing	2.0	1	Mat	Severe surface porosity; medium intergranular fissuring
70	1170		Reducing	2.0	1	Mat	Severe surface porosity; severe intergranular fissuring
56*	1170		Reducing	2.0	4	Mat	Severe surface porosity; severe intergranular fissuring
57*	1170		Reducing	2.0	3	Mat	Severe surface porosity; severe intergranular fissuring
90	Commercial A		Oxidizing	1.0	19	Semimat	Surface zone of fine porosity; no intergranular fissures
91	Commercial B		Oxidizing	1.0	17	Semimat	Surface zone of fine porosity; no intergranular fissures
92	Commercial A		Reducing	1.0	6	Mat	Surface zone of voids; slight intergranular fissuring
94	Commercial B		Reducing	1.0	7	Mat	Medium surface porosity; slight intergranular fissuring
95	1170		Oxidizing	0.9	19	Semimat	Slight surface porosity; no intergranular fissures
96	1170	Oxyhydrogen	Oxidizing	0.9	18	Bright	Slight surface porosity; no intergranular fissures
97	1170		Oxidizing	2.0	14	Mat	Severe surface porosity; medium intergranular fissuring
58*	1170		Reducing	2.0	4	Mat	Medium surface porosity; severe intergranular fissuring
37	1170		Reducing	0.9	2	Mat	Severe surface porosity; severe intergranular fissuring
	Commercial A				19		Results of bend tests of original strip after annealing
	Commercial B				10		
					17		

* Preliminary test runs with less accurate control of flame conditions. ^a Inner cone of flame brought close to sample (distance $\frac{1}{8}$ in.). ^b Samples were light violet color due to superficial oxidation during cooling; mat surface remained dull and bright surface was unchanged after reduction of the oxide film in warm 5 per cent formic acid.



FIG. 2.—RUTHENIOPALLADIUM (No. 1170) HEATED IN NEUTRAL (OR OXIDIZING) OXYACETYLENE FLAME. DUCTILITY: 24–29 BENDS.

FIG. 3.—RUTHENIOPALLADIUM (No. 1170) HEATED IN REDUCING OXYACETYLENE FLAME. DUCTILITY: 20–21 BENDS.

FIG. 4.—COMMERCIAL RUTHENIOPALLADIUM (A) HEATED IN OXIDIZING OXYACETYLENE FLAME. DUCTILITY: 18 BENDS.

FIG. 5.—COMMERCIAL RUTHENIOPALLADIUM (A) HEATED IN REDUCING OXYACETYLENE FLAME. DUCTILITY: 16 BENDS.

All $\times 500$. Electrolytic etch (a.c.). External surface at top.

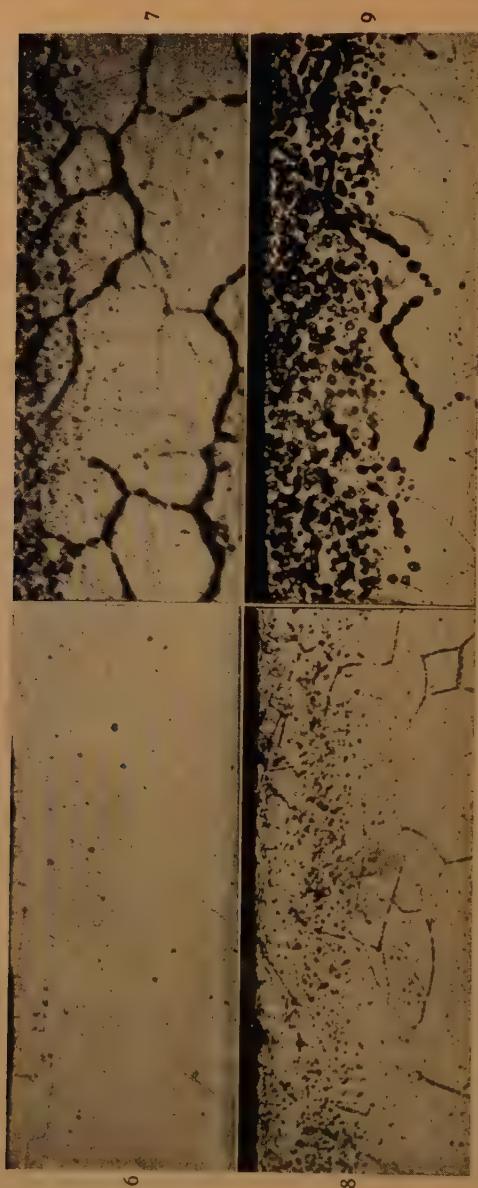


FIG. 6.—RUTHENIOPALLADIUM (No. 1170) HEATED IN OXIDIZING OXY-CITY-GAS FLAME. DUCTILITY: 19-20 BENDS.
 FIG. 7.—RUTHENIOPALLADIUM (No. 1170) HEATED IN REDUCING OXY-CITY-GAS FLAME. DUCTILITY: 1-4 BENDS.
 FIG. 8.—COMMERCIAL RUTHENIOPALLADIUM (A) HEATED IN OXIDIZING OXY-CITY-GAS FLAME. DUCTILITY: 19 BENDS.
 FIG. 9.—COMMERCIAL RUTHENIOPALLADIUM (A) HEATED IN REDUCING OXY-CITY-GAS FLAME. DUCTILITY: 6 BENDS.
 All $\times 500$. Electrolytic etch (a.c.). External surface at top.

samples (Fig. 7) and 1.5×10^{-3} in. in the commercial samples (Fig. 9).

In order to get the best results with the oxidizing oxy-city-gas flame, certain

flame the pure metal became seriously embrittled and acquired a mat surface accompanied by a porous subsurface zone 0.6×10^{-3} in. deep, with a few inter-



FIG. 10.—RUTHENIOPALLADIUM (NO. 1170) HEATED IN OXIDIZING OXYHYDROGEN FLAME. DUCTILITY: 18-19 BENDS.

FIG. 11.—RUTHENIOPALLADIUM (NO. 1170) HEATED IN REDUCING OXYHYDROGEN FLAME. DUCTILITY: 4 BENDS.

Both $\times 500$. Electrolytic etch (a.c.). External surface at top.

precautions must be observed, the total effect of which limits its usefulness. For instance, samples heated with a torch having an orifice of 2-mm. diameter, and hence more voluminous flame, showed lower bend-test values than similar samples heated in smaller flames obtained with orifices 0.9 and 1.0 mm. in diameter, respectively (Table 1). Also, placing a sample too near the tip of the inner cone of an oxidizing flame caused serious loss of ductility accompanied by porosity and intergranular fissures (sample 88, Table 1). Cooling in city gas instead of in air did not further affect the ductility of rutheniopalladium but it caused deterioration of the surface, probably due to carbonizing; quenching in water instead of cooling in air lowered the ductility, and continuous heating appeared to damage the metal more than intermittent heating.

Palladium behaved similarly to rutheniopalladium; in the reducing oxy-city-gas

granular fissures deep inside the metal; in the oxidizing flame the metal suffered only slight loss of ductility and there was only slight subsurface porosity.

A borated oxy-city-gas flame provided by passing the city gas through methanol saturated with anhydrous boric acid (boric anhydride) gave results that were identical with those already obtained for rutheniopalladium heated in the unborated oxy-city-gas flame, except that the layer of fused boric anhydride that formed on the heated surface helped to maintain brightness.

Oxyhydrogen.—Samples heated in the oxidizing flame remained ductile, two out of three remained bright and all showed fine subsurface porosity (Fig. 10). Samples heated in the reducing flame were seriously embrittled and showed considerable subsurface porosity with intergranular fissures to a depth of 2.5×10^{-3} in. (Fig. 11), accompanied by loss of brightness.

Oxy-carbon Monoxide.—Samples heated in the oxidizing and reducing oxy-carbon monoxide flames behaved like those heated in the corresponding oxy-city-gas and oxy-hydrogen flames. Data have been omitted for the sake of brevity.

Absence of Hot Shortness.—The question arose as to whether loss of cold ductility was accompanied by hot shortness, especially in metal heated in an oxy-city-gas flame, which contains significant amounts of sulphur compounds. Tests on samples heated in a reducing oxy-city-gas flame (severest of all tests) disclosed that the loss of cold ductility was not accompanied by hot shortness.

EFFECT OF OXYACETYLENE FLAME ON SOLDERS

Preliminary Soldering Tests.—As jewelry manufacturers have used the same solders, the so-called platinum solders, and the same flame, oxy-city gas, for soldering palladium and its alloys as have been used for platinum, it might be assumed that this flame would not cause embrittlement of platinum solders and that the oxy-acetylene flame would be even less likely to do so. Nevertheless, as a precaution, the behavior of platinum solders in an oxyacetylene flame has been examined and a few soldering tests have been made.

The platinum solders, obtained from Baker and Company, were in the form of 0.010-in. strip, and included a range of alloys with different melting points suitable for the various soldering operations in the manufacture of palladium jewelry, as follows:

GRADE OF SOLDER	MELTING POINT, DEG. C. (NOMINAL)	
Hard*.....	1400	} generally used with palladium
Medium Hard*.	1300	
Medium*.....	1200	
Soft.....	1100	
Extra Soft.....	1000	

* These solders are based on the palladium-gold series of alloys. Detailed compositions have not been published.

The soldering test was performed by placing together two pieces of laboratory rutheniopalladium (No. 1170), each $\frac{1}{4}$ by $\frac{3}{16}$ by 0.010 in., on an alundum support and laying small pieces of the solder on the joining line, then heating with a neutral oxyacetylene flame, using the small tip (orifice 0.4-mm. dia.) until the solder melted and covered the joint; this was repeated on the other side. A sample was soldered without difficulty with each of the solders listed above. All the solders (including the hard and medium hard grades) flowed satisfactorily. The samples were then given the regular cold-bend test, to determine the effects on the ductility of the metal. There was no evidence of loss of ductility either at the joint or in the adjacent metal.

Samples of the 1400 (hard) solder were tested after heating in oxidizing and reducing oxyacetylene flames, respectively. There was no loss of ductility of the solder and microexamination disclosed that no impairment had occurred in either flame. Another piece of solder was cut in two by an oxyacetylene flame, welded together again and tested for ductility; there was no embrittlement.

These brief tests indicated that the oxy-acetylene flame can be used without fear of bad effects on the regular platinum solders. Furthermore, experience shows that more use can be made of the hard solders, because the heat is confined to a smaller area of the work and can be better controlled. This will be an advantage because the soft grades are said to "burn" in oxidizing flames.

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DISCUSSION

(C. S. Smith presiding)

F. E. CARTER.*—It is well known that the platinum metals react with carbon to form carbides; it is not necessary to reach the melting points of the metals for the reaction to occur. Since the oxyacetylene flame was so rich in carbon, this has always been considered particularly dangerous to use for heating the platinum metals except with a flame that was distinctly oxidizing; preferentially oxy-city gas or oxyhydrogen has been used. The authors have shown that the fear was unfounded, at least up to the welding or soldering temperatures, and there can be little doubt that the embrittlement is due to the reaction between dissolved oxygen and absorbed hydrogen.

The paper gives a simple method for determining ductility of a metal or alloy that may be usefully employed by the practical man. Since this is a good practical paper, it seems somewhat unfortunate that the impression may be gained that helium is necessary for the annealing atmosphere; it is true that the results were confirmed with commercial samples of rutheniopalladium, but in these cases it is not clear whether or not they too were annealed in helium. I think it should be stated specifically that in commercial practice helium annealing is not essential.

Since the paper states that the type of flame employed is very important, it might be well to give sketches of the different flames; the practical man would be happier to see, rather than to read, the structure of the oxidizing, neutral and reducing flames.

As far as brittleness is concerned, the described semiquantitative results apply only to samples of the thicknesses specified; however, the depth of the subsurface porosity is, as shown, slight and would affect the ductility only to a small degree with samples thicker than those described in the paper. With thinner samples the differences in the results would be much greater than those given, indicating that the authors' findings will be highly valuable when thin stock is being handled. On the other hand, the surface appearance of the palladium is improved by the use of the oxyacetylene

torch on any size of sample, and this is an observation that is well worth while.

R. H. ATKINSON and G. P. GLADIS[†] (authors' reply).—All samples, including the commercial samples, were annealed in helium to remove free oxygen before they were submitted to the flame test. The authors did not intend to convey the impression that helium annealing should be used in commercial practice.

The authors decided against including sketches of the different types of oxyacetylene flame and instead would refer those interested to the booklets published by the suppliers of acetylene. If a demonstration of the different types of flame can be arranged, so much the better.

Dr. Carter appears to have assumed that the depth of the subsurface porosity was a measure of the loss of ductility. It would be misleading to look upon embrittlement as being restricted to the zone of subsurface porosity when in fact it often extended right through the samples (0.02 in. thick). Consequently, though the damage done by unsuitable flames might be somewhat less in thicker samples, still it would be serious.

P. A. BECK.*—How is it possible for oxygen to penetrate into samples heated in some of the reducing flames; e.g., oxygen, city gas and oxyhydrogen? Does the oxygen get in when the samples are being heated up?

R. H. ATKINSON.—It is difficult to understand how oxygen and hydrogen could penetrate simultaneously into the hot metal unless it meant that both these gases were present in the flame in immediate contact with the metal, thereby indicating that the flame had not reached a state of equilibrium. Further experiments will be necessary to test this view. It is unlikely that oxygen was diffused into the samples when they were being heated up because the time interval was too short.

MEMBER.—Was any oxygen present in the samples originally?

R. H. ATKINSON.—All samples were previously annealed in helium to free them from oxygen.

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Effect of Copper and Some Other Metals on the Gold-germanium Eutectic

BY ROBERT I. JAFFEE,* JUNIOR MEMBER, AND BRUCE W. GONSER,† MEMBER A.I.M.E.

(Chicago Meeting, February 1946)

RECENT work by the authors¹ established the constitutional diagram of the gold-germanium system. Of particular interest in the simple eutectiferous system was the eutectic alloy at 12 per cent Ge, which melted at the very low temperature of 356°C. and had an unusually fine eutectic structure. It was of interest to investigate the effect of third components on the melting point, microstructure, and strength of this alloy, and in this work the effect of copper is discussed rather completely, with less complete data on the effects of silver, platinum, nickel, and zinc. No reference in the literature has been found on ternary systems with gold-germanium.

MATERIALS AND ALLOYING

As in the work on the binary system, gold-germanium, the germanium used in this investigation was the cyanide-reduced, 99.9 per cent product, produced by the Eagle-Picher Co. Fine gold sheet from Handy and Harmon, pure platinum sheet from the American Platinum Works, copper magnet wire from Anaconda, nickel wire assaying 99.6 per cent Ni, and electrolytic zinc were used for alloying. To make the alloys, charges of the pure metals were put in a graphite crucible and melted in an atmosphere of pure hydrogen. The

temperature was brought up to about 1050°C., and the metal allowed to freeze in the crucible. Except with alloys containing zinc, melting losses were consistently less than a few milligrams.

When zinc was a component, weight losses up to half the weight of the zinc present were incurred, and the alloy compositions were calculated by assuming the entire weight loss to be that of zinc. In all other cases the composition of the alloys could safely be taken as that of the charge. The ingots, as solidified, were segregated, the heavier primary phases being at the bottom and sides of the ingots and the lighter primary phases at the top, but by sectioning the entire ingot vertically for microscopic examination, this factor could be evaluated. Ingots for microscopic examination weighed one gram, and those for thermal analysis weighed three grams.

THERMAL ANALYSIS

In this work, the eutectic line composition and thermal arrests were desired, and, after microscopic exploration had established the position of the eutectic line at a given percentage of the third component, a thermal analysis was run at that composition. The method of thermal analysis used in the work on the binary Au-Ge system,¹ a method particularly well suited for a small quantity of material, was used in this work. Clearly defined arrests were obtained, although with some alloys containing platinum

Manuscript received at the office of the Institute Nov. 26, 1945. Issued as T.P. 1998 in METALS TECHNOLOGY, April 1946.

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¹ References are at the end of the paper.

or nickel undercooling was observed. Calibrated 28-gauge chromel-alumel thermocouples, checked at the lead and zinc points, were used for the temperature

compositions and freezing points of eutectic-line alloys at 2.5, 5, 10, 20, and 30 per cent Cu. These data show that the eutectic valley proceeds away from the

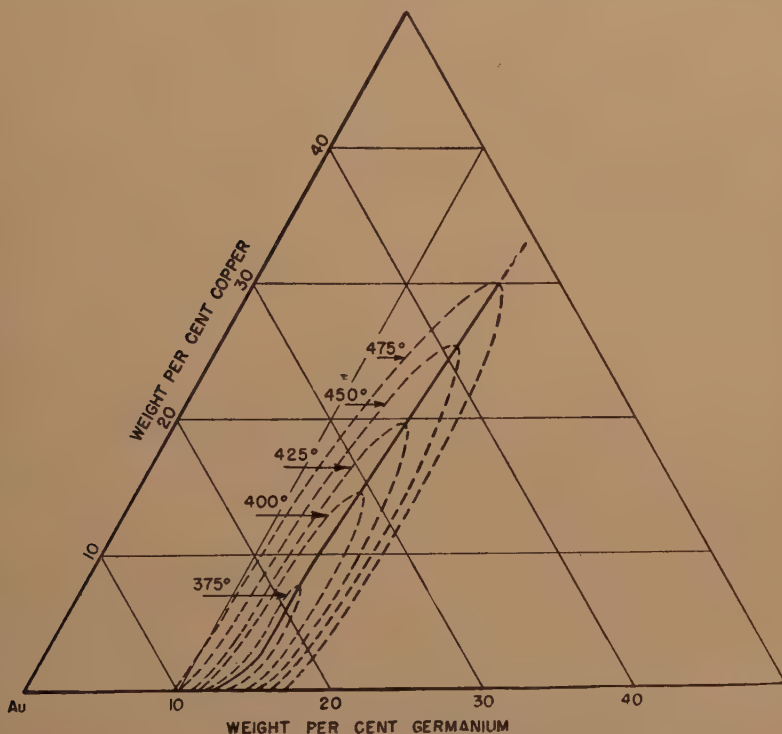


FIG. 1.—EUTECTIC LINE (SOLID LINE) IN GOLD-COPPER-GERMANIUM ALLOY WITH ESTIMATED ISOTHERMS (DOTTED LINES).

measurement. Values of the eutectic line arrest are considered accurate to within $\pm 2^\circ\text{C}$.

COPPER-GOLD-GERMANIUM ALLOYS

Diagram

The eutectic line in the Au-Cu-Ge system from the Au-Ge binary eutectic has been traced to 30 per cent Cu, and the freezing points of alloys along that line have been determined. Fig. 1 shows the location of the eutectic line and estimated isotherms connecting the known temperatures along the eutectic line with the known liquidus curve of the Au-Ge binary system. Table 1 gives

binary eutectic at substantially constant germanium content and at increasing temperatures.

Previous data by the authors¹ and by Owen and Roberts³ show that there is very little solubility of germanium in gold. Germanium is soluble in copper to about 10 per cent at room temperature.⁴ It appears probable that some germanium is dissolved in the copper-gold phase, which may account for the slight shift of the eutectic line to higher germanium percentages.

X-ray

Microscopic evidence indicates that two phases are present in the alloys:

gold-copper solid solutions and free germanium. At the high copper contents the solid solution phase exhibited coring,

Johansson and Linde,³ and is shown for purposes of comparison with the pattern of the new phase found.

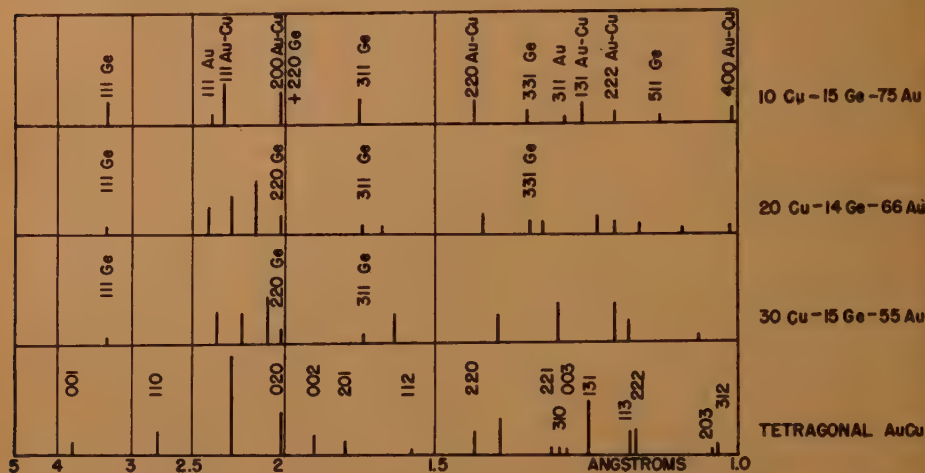


FIG. 2.—X-RAY PATTERNS¹ OF GOLD-COPPER-GERMANIUM ALLOY WITH ORDERED TETRAGONAL GOLD-COPPER SHOWN FOR COMPARISON.

indicating that it froze over a considerable temperature and composition range. X-ray data show that free germanium is present as one of the phases up to 30 per cent Cu. At 10 per cent Cu the Au-Cu phase is disordered face-centered cubic of $a_0 = 4.00\text{\AA}$, with a few very faint lines of gold. The fact that diffraction lines were diffuse, and that free gold was shown in the photograms, is further indication that the gold-copper phase froze over a composition range extending to pure gold. At 20 and 30 per cent Cu, the lines of the second phase did not correspond to the disordered cubic or to the ordered Au_3Cu or AuCu phases. This new, second phase was in evidence both when the alloy was cast and slowly cooled and when it was quenched in water while still molten. Fig. 2 is a graphical representation of the X-ray data, in which the abscissa gives the interplanar spacing in Angstrom units, and the ordinates give the relative intensities of the diffracted lines. The pattern for the ordered tetragonal AuCu structure was taken from

Microstructure

As copper increases, the extremely fine eutectic structure, which was evident in the binary eutectic, appears to be coarsened appreciably, and the germanium phase in the eutectic appears to change its habit from particles to rods or platelets. Figs. 3 to 8 show microstructures of the eutectic-line alloys. At 2.5 per cent Cu, the structure is still fairly fine, but the beginning of the coarsening and change of crystallization habit is apparent. Indication that the crystallization habit of germanium becomes platelets may be seen in Fig. 5, where one is shown sectioned through its plane.

Mechanical Properties

Hardness values (Table 1) indicate that the coarsening of the eutectic structure by copper additions is accompanied by slight increase in hardness to 10 per cent Cu. At 20 to 30 per cent Cu the hardness jumps almost 100 points. This probably is caused by the new matrix phase, which was shown by X-ray evidence. Tensile-



FIGS. 3-8.—EUTECTIC-LINE ALLOYS OF GOLD-COPPER-GERMANIUM ALLOYS.

Fig. 3. 12 per cent Ge, 88 Au. Binary eutectic. $\times 1000$.

Fig. 4. 2.5 per cent Cu, 14 Ge, 83.5 Au. $\times 500$.

Fig. 5. 5 per cent Cu, 14 Ge, 81 Au. $\times 500$.

Fig. 6. 10 per cent Cu, 14 Ge, 76 Au. $\times 500$.

Fig. 7. 20 per cent Cu, 15 Ge, 65 Au. $\times 500$.

Fig. 8. 30 per cent Cu, 16 Ge, 54 Au. $\times 500$.

strength data were obtained from butt joints of 0.020 in., 18-kt. gold strip soldered with the Au-Cu-Ge alloys. These values (Table 1) are not true tensile strengths

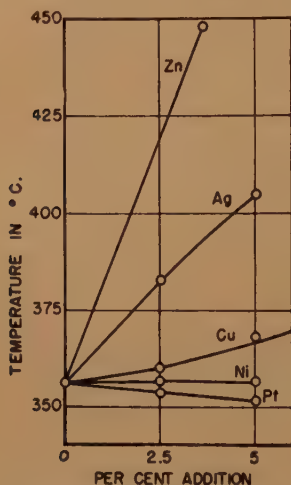


FIG. 9.—EFFECT OF ADDITIONS ON FREEZING POINT OF GOLD-GERMANIUM EUTECTIC.

of the materials tested, but it is believed they approximate the true values. Pure eutectic, tested in tension by conventional means, had a tensile strength of 55,600 lb. per sq. in., and a butt joint made with eutectic Au-Ge had a strength 53,000 lb. per sq. in., indicating that the approximation is fairly good. Up to 20 per cent Cu the tensile strengths are slightly higher than the value for the binary eutectic, but appear to fall off at 30 per cent Cu. Elongations of the alloys are negligibly small.

TABLE 1.—Properties of Au-Cu-Ge Alloys

Composition, Weight Per Cent			Eutectic-line Arrest, Deg. C.	Vickers Hardness ^a	Strength, ^b Lb. per Sq. In.
Cu	Ge	Au			
0	12	88	356	205	53,000
2.5	14	83.5	360	218	53,500
5	14	81	368	230	61,000
10	14	76	385	270	61,000
20	15	65	430	312	62,500
30	16	54	477	290	40,000

^a Diamond pyramid, 5-kg. load.

^b Taken from butt joints of 18-kt. gold strip soldered with these alloys.

Color

Estimation of the color of the alloys is difficult, but the addition of copper to eutectic Au-Ge appears to decolorize it somewhat. The actual degree of decolorization may be taken from the observation that the binary eutectic appears similar to yellow 18-kt. jewelry gold, and the 30 per cent Cu eutectic-line alloy appears to have the pale gold color of some 12-kt. jewelry gold.

Applications

Soldering of gold-base alloys, gold-plated articles, and copper-base alloys may readily be done with the Au-Cu-Ge eutectic-line alloys, using conventional soft-solder or hard-solder fluxes and torch or furnace methods. The fluidity and wetting properties of the Au-Ge eutectic are slightly reduced by the copper additions. Like the binary Au-Ge eutectic, these alloys also expand on solidification and have been used for precision casting, as for inlays in dental work.

OTHER TERNARY ALLOYS WITH GOLD-GERMANIUM

Compositions and freezing points of alloys of silver, zinc, nickel, and platinum with Au-Ge, which are either eutectic-line

TABLE 2.—Properties of Alloys of Au-Ge with Other Metals

Composition, Weight Per Cent			Eutectic-line Arrest, Deg. C.	Vickers Hardness ^a	Strength, ^b Lb. per Sq. In.
Addition	Ge	Au			
2.5 Ag	13.5	84	383	149	52,000
5 Ag	14	81	405	156	
3.6 Zn	15.3	81.1	448	170	
2.5 Pt	13.5	84.5	354	145 ^c	55,000
5 Pt	14	81	352		
2.5 Ni	13	84.5	357	110 ^c	41,500
5 Ni	15	80	357		

^a Diamond pyramid, 5-kg. load.

^b Taken from butt joints of 18-kt. gold strip, soldered with these alloys.

^c Taken in fine structure, with diamond pyramid and 1-kg. load.



FIGS. 10-15.—EFFECTS OF VARIOUS ADDITIONS. ALLOYS AS CAST.

Fig. 10. 5 per cent Ag, 18 Ge, 77 Au. Unetched. $\times 500$.

Fig. 11. 3.6 per cent Zn, 15.3 Ge, 81.1 Au. Unetched. $\times 300$.

Fig. 12. 7.5 per cent Pt, 10 Ge, 82.5 Au. Unetched. $\times 50$.

Fig. 13. 10 per cent Pt, 15 Ge, 75 Au. Unetched. $\times 50$.

Fig. 14. 5 per cent Pt, 17 Ge, 78 Au. Unetched. $\times 500$.

Fig. 15. 5 per cent Ni, 15 Ge, 80 Au. Unetched. $\times 300$.

alloys or which contain a predominance of fine structure, are given in Table 2. The relative effect of the various additions on the freezing point of the Au-Ge eutectic is shown graphically in Fig. 9, where it is indicated that silver, zinc, and copper raise the freezing point while platinum lowers the freezing point and nickel seems to have no effect.

Silver and Zinc

Silver and zinc appear to act on the Au-Ge eutectic in the same way as copper, but much more drastically. The increase in the eutectic-line arrest is particularly marked, and the alloys appear to have a long, mushy range down to the binary eutectic temperature. Coarsening of the eutectic structure is shown by Figs. 10 and 11. There are only two phases in these alloys: alpha-gold solid solutions and germanium.

Platinum

Ternary alloys with platinum have peculiar microstructures comprising primary alpha dendrites, primary germanium, and fine eutectic structure. Figs. 12 and 13 show rows of massive, primary germanium against a background of alpha dendrites and eutectic. This behavior was noted by Davidson for the Bi-Sn eutectic, where both primary tin dendrites and primary bismuth were present with eutectic at the eutectic composition.⁵ Davidson ascribed the anomalous behavior to undercooling. An X-ray pattern for an alloy of 5Pt-14Ge-81Au showed lines of an Au-Pt phase of lattice constant 4.075\AA . and the diamond cubic germanium phase of lattice constant 5.65\AA ., plus two very faint lines (d values 2.23 and 2.10\AA .) from an unidentified phase. The explanation of undercooling for the anomalous presence of both primary phases with the eutectic appears well founded, since the 2.5 and 5 per cent Pt alloys undercooled about 12°C . at their eutectic arrests. The range over which the

phenomena take place is surprising, however. It is probable from the X-ray evidence of a third phase, and from the lowering of the eutectic arrest, that there is a ternary eutectic in this system.

Nickel

Like the platinum ternary alloys, Au-Ge-Ni alloys near the eutectic show the presence of primary germanium with the eutectic structure. X-ray patterns gave lines for both alpha gold and germanium, plus two lines (d values 1.915 and 1.048) of an unidentified third phase. It is probable that there is a ternary eutectic in this system, too, because of the X-ray indication of a third phase, the slight effect on the eutectic arrest, and the fact that the Vickers hardness of the fine structure is only 110, compared with 200 for the binary eutectic. Fig. 15 shows the microstructure of a typical Au-Ge-Ni alloy near the eutectic line. The micrograph was photographed in polarized light, 5° from crossed nicols, and with this illumination the germanium phase showed some anisotropy. Primary germanium in Au-Ge does not show any anisotropy, and it is possible that some nickel has dissolved in the germanium to bring it about.

CONCLUSIONS

1. The eutectic valley in the Au-Cu-Ge system from the binary Au-Ge eutectic has been traced to 30 per cent Cu. Up to 10 per cent Cu the phases in the eutectic line are face-centered cubic Au-Cu solid solutions and free germanium. At 20 per cent Cu, the phases are free germanium and a new phase, which could not be identified. Coarsening of the eutectic structure by copper has been noted. Hardnesses from 200 to 300 Vickers, strengths of about 55,000 lb. per sq. in., and some applications of these alloys have been reported.

2. Silver and zinc sharply raise the temperature of the eutectic valley. Hardnesses of about 150 Vickers, and strength

of about 50,000 lb. per sq. in. have been reported.

3. Platinum and nickel ternary alloys with Au-Ge apparently undercool to give microstructures of primary germanium and primary alpha dendrites over a rather wide range of composition. The freezing point of the eutectic line is lowered by platinum and nickel, and it is believed that ternary eutectics may occur in these two systems.

ACKNOWLEDGMENTS

The authors are indebted to the Eagle-Picher Company for permission to publish these results, and to E. W. McMullen, of

the same company, for his excellent cooperation.

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Symposia

Symposium on Extrusion

(New York Meeting, October 1945)

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The Extrusion Process

BY W. W. COTTER* AND W. R. CLARK,† MEMBER A.I.M.E.

WEBSTER tells us the word "extrude" means to "force, press or push out; to protrude." As applied to the metal industry, the process consists largely of forcing plastic elements (plasticity usually obtained by preheating), through dies of predetermined profiles, into constant sections of considerable length and weight.

Most of the "virgin" metals are quite malleable under this process, likewise many of the commonly used "alloys" in various industries, when basic elements are proportioned or combined within the natural laws and limits of good metallurgy. Several of the foundry alloys, both ferrous and nonferrous, together with some of the heat-treatable light metal mixtures, are decidedly weak and hot short at ordinarily plastic ranges, and consequently are troublesome or quite incapable of commercial extrusion.

DEVELOPMENT OF PROCESS

This process was conceived some time before 1800 and during its first century was employed almost entirely in making

lead pipe, plumbing fittings and coating electrical cables. As a result of contact and experience with the lead industry and presses, Alexander Dick, of London, England, is credited with first having applied the principles of extrusion to brass, and in 1894 brought out a 500-ton horizontal press powered by hydraulics. A duplicate of this unit was imported by one of the Connecticut brass mills and was in experimental operation by 1900. During the first five years of operation, this press proved the value of the method to American industry, as it immediately revolutionized and converted the manufacture of brass rod from a 15-pass cold-rolling operation, with elimination of several intermediate anneals and cleanings, to an extrusion and a finishing draw. Likewise, ornamental brass and bronze moldings formerly cast and machined were produced in one squeeze on the extruder. The extrusion operation, being entirely that of compression, deforms the material without tensile stresses and can be used on delicate mixtures under heat, which cannot be hot-worked by straight hot-rolling or roller piercing.

Base slabs of clock-brass strip were early in line of development or improvement, as were the brass bronzes (Naval brass, Muntz metal, manganese bronze, and

Manuscript received at the office of the Institute Nov. 13, 1944. Listed for New York Meeting, February 1945, which was canceled. Issued as T.P. 1850 in METALS TECHNOLOGY, September 1945.

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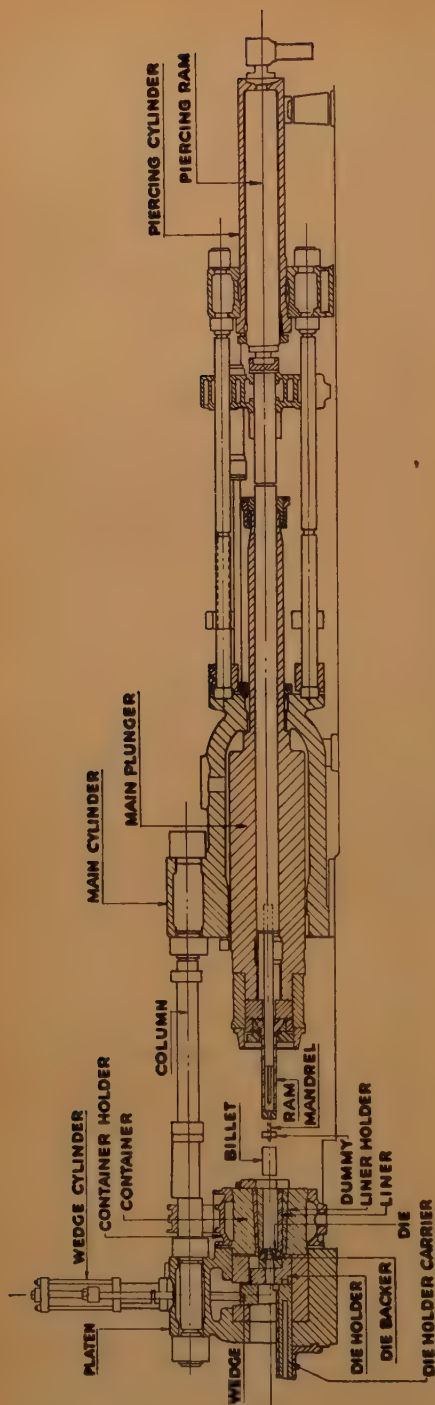


FIG. 1.—TUBE EXTRUSION PRESS.

others), popular as engineering materials for bolt stock, as well as structural shapes for marine and other mild conditions of corrosion.

By 1910, American engineers undertook to design tube shell extruders, but were unsuccessful. The first World War began before fabricators could procure the more substantial designs of tube extruders produced in Germany; and it was not until the middle twenties that better models of the Universal extruders (double-actioned presses), equipped with hydro-pneumatic accumulator systems and other modern equipment, were available in the United States.

America by this time was fast becoming extrusion minded. Both the brass industry and the light-metals industry had operated during the first World War with ordinary rod extruders of 1000 to 2000-ton capacities; but following this event, the aluminum plants led the field with higher capacities and much more versatile equipment. By the late thirties, industry as a whole had a choice of high-powered, standardized and proven designs of extruders for any practical application. At the present time, American industry, including Government-owned and sponsored installations, has upward of 200 units supporting the war effort.

The scope of this paper is confined to extrusion of plain and tubular sections of copper-base alloys. A broad treatment of the whole subject is available in an English book written by Claude E. Pearson.¹

EXTRUSION MACHINES

The standard extrusion machine is built in two general styles; one a double-action machine, which is generally used in the extrusion of tube and has the advantage in rod extrusion of a higher pressure, which may be exerted on the ram when pressure is applied to both plungers; and the other, a

¹ References are at the end of the paper.

single-action machine, which is normally used in the extrusion of rod and seldom used in the extrusion of tubes. Machines having a pressure capacity in excess of 1200 tons are usually horizontal. The use of smaller vertical machines is confined to the manufacture of tubing. While many vertical machines are used abroad, few are in operation in this country, owing to their limited capacity.

Terminology

Billet.—Material to be extruded, usually round, in section and of a length from 1 to 4 times its diameter.

Container.—Cylinder that contains the billet during extrusion.

Ram.—Plunger that exerts the pressure on the billet through the dummy.

Dummy.—The dummy is interposed between the ram and the billet. It is slightly larger than the ram, to ensure proper clearance so that the ram may be easily retracted. It also acts as a heat absorber in keeping the end of the ram from overheating.

Die.—Perforated shaped plate through which the metal is extruded.

Mandrel.—Plunger (usually slightly tapered) that pierces the billet in tube extrusion and determines the inside diameter of the tube.

Die Backer.—Transmits the pressure exerted on the die to the die head. It has a hole slightly larger than the die. Both die and backer are held in the die holder, which in turn is held in the head.

Die Head.—The die head, or holder, is locked against the container during extrusion by the wedge, and after extrusion is withdrawn to permit removal of butt and shell, and to sever these from the extruded shape.

Butt.—The butt, or stump, is the unextruded portion of the original billet left adjacent to the die.

Shell.—The shell is the thin part of the billet left in contact with the container

because of a difference in diameter of the dummy and the container bore.

Fig. 1 shows in simplified form the tools, tool holders, and essential elements used in the horizontal extrusion press. The only difference between the double-action machine and the single-action machine is elimination of the piercing cylinder and plunger, and the use of a solid ram instead of the hollow ram shown, through which the piercing mandrel operates. Water for hydraulic pressure is supplied usually by a pump and accumulator system, at pressures from 3000 to 5000 lb. per sq. in. In addition to the high-pressure hydraulic system, a low-pressure pre-filling system is generally used for idle stroking of the ram, in order to conserve high-pressure water.

THE PROCESS

In the normal extrusion of brass and copper alloys, the actual extrusion time usually is from 30 to 45 per cent of the total cycle between billets, so that a direct-acting pump would be operating against pressure less than half the time. Smaller pumps can be used with the accumulator system, and the control of speed of extrusion, which is possible with the accumulator system, is necessary with some of the more delicate alloys.

The container that holds the hot billet during the extrusion operation is usually built up in three sections; (1) the liner, of a hard, high-heat-resisting alloy such as chrome-tungsten steel; (2) the bushing surrounding the liner, of a high-strength, tough alloy, such as 0.70 per cent C, 1.45 Cr, 0.45 Mo, 0.20 Va, with a medium degree of heat resistance and heat-treated to Brinell 300 to 330; and (3) the outer ring of the container itself, of S.A.E. 4340 steel forging heat-treated to Brinell 260 to 300. This is set into a container holder, which has a passage containing gas burners so that the container may be preheated and kept warm from the outside

during the extrusion operation. It is also desirable to introduce a gas burner and apply heat to the interior of the container liner for a sufficient time before the machine is placed in operation to reach the normal working temperature, which varies with the alloy to be extruded.

Hot billets are supplied from a continuous heating furnace, and in the modern machines are conducted by a conveyor to an elevator that places them in alignment with the container into which they are introduced by the ram.

The container usually is bolted to the head of the press, which contains a hole of sufficient size to permit the die head to be entered and withdrawn from the extruding position during each extrusion cycle, in order that the unextruded stump remaining can be severed and removed from the extruded section. When the die head is in the extruding position, it is locked by a wedge, usually operated vertically by means of a hydraulic cylinder. An additional cylinder is used to move the die head in and out of the extruding position. In the die head is placed the die and the die backer. The latter has a hole slightly larger than the die opening and its use permits the use of a much smaller, and, therefore, less expensive die.

Not all of the metal in the billet, when extruded, appears as good material. From 15 to 25 per cent is normally discarded. When some of the oxidized surface of the hot billet is drawn into the stream of extrusion, it does not reweld to the clean material, and any section of the extruded material containing this defect must be discarded.

In ordinary brass extrusion, the practice of using a dummy between the ram and the hot billet, of somewhat smaller diameter than the container liner, is quite common. After it has upset the billet to fill the container, it broaches the clean material from the interior of the billet, leaving a thin shell of oxidized material in

the container liner, which is removed by a second stroke of the press (largely with low-pressure water) through the insertion of a larger cleanout dummy. When the unextruded length of the billet is reduced to from 7 to 10 per cent of its original length, some of the oxidized material from the two ends usually finds its way into the extruded section, and there is no object in carrying extrusion further.

After the billet is elevated in line with the container, and the die has been placed in position by the cylinder operating the die head, and has been locked in this position by the wedge, the billet is introduced into the container, the ram withdrawn, and the dummy placed in line with the container, usually by an elevator from below the machine. The ram and dummy are then moved forward with low-pressure water by the main plunger until they contact the hot billet. The billet preferably should be within $\frac{1}{4}$ in. of the diameter of the container, as less scrap will be made than when it is smaller.

In the extrusion of tubes, it is quite essential that the billet be upset by the main ram until it fills the bore of the container, the main ram then being withdrawn sufficiently to create clearance for back flow of material when the piercing ram is stroked to pierce the billet preparatory to tube extrusion. Prefilling the container in this way is quite essential in order to complete the upward flow of the metal in the billet from the lower side of the container before introduction of the piercing ram. The completion of this flow also results in a more uniform chilling of the thin shell of the hot billet on all sides through pressure contact with the container liner. This chilling helps to center the dummy during extrusion and tends to leave a shell of uniform thickness, thus preventing the oxidized surface metal from entering the die during the earlier stages of extrusion.

After completion of the extrusion stroke, the wedge is released, the die head with-

drawn, and the butt is severed from the rod by a shear or saw, while a second dummy is elevated into position and pushed through the container in order to remove the oxidized shell from it. This shell is then discarded and any scrap particles remaining are cleaned out before the die head is placed again in position for the next extrusion. During this interval, the piercing mandrel, if used, is cooled with a water spray and then wiped off clean with an oily rag.

Copper-base Alloys

There are several important differences in the extrusion of copper-base alloys versus aluminum and magnesium. These can best be expressed by differences in temperature and speed—temperatures both of material to be extruded and of the tools involved. In the extrusion of light alloys, tool temperatures must be maintained within narrow limits, and even so the rate of extrusion of the more delicate alloys is very slow compared with that used in the copper-base alloys, because, with too rapid extrusion, cracking takes place in the extruded product.

Many of these alloys can be extruded but cannot be hot-worked in any other way because tensile stresses set up in these materials during the hot-working operation produce cracking or rupture. There is also a distinct limitation of the range of hot-workability; that is, the difference between the minimum and maximum temperature between which the material can be deformed without excessive pressure on the lower side or incipient melting on the upper. Furthermore, on materials presenting high resistance to deformation under most favorable conditions, the rise in temperature at the point of deformation due to the transformation of the energy expended in the deformation into work heat may result in raising the temperature of the material sufficiently to cause incipient melting of the extruded material

as a whole, or in combination with friction heat between the material and die, in overheating the surface so that cracking takes place. Slower extrusion will reduce this tendency, through the transfer of more of the work heat by conductance to the cooler portions of billet and die.

The pressure on the dummy necessary to extrude varies with the alloy, the speed of extrusion, temperature of material, temperatures of container, die, and dummy, ratio of dummy area to die area (or areas if multiple dies are used), and the length of the billet (if greater than its diameter).

The starting pressure at normal rates of extrusion is usually the maximum, partly because after extrusion starts the part of the billet that is being deformed by extrusion through the die is raised in temperature through the transformation of work into heat. The transfer of this heat to adjacent material in turn raises its temperature and reduces its resistance to deformation in approaching the die.

The approximate theoretical temperature rise due to this work heat is given below. It has been shown that work done (neglecting surface friction) in deforming plastic material by elongation is equal to

$$iV \log_e \frac{A}{a} \quad \text{or} \quad iV \log_e \frac{l}{L}$$

where i is the pressure necessary to overcome the resistance of the material at any given speed and temperature to deformation, in lb. per sq. in.

V , the volume of material displaced,

A , the initial area,

a , the final area,

L , the initial length,

l , the final length.

In extrusion, the work done per inch of ram stroke is PA inch-pounds where P is the pressure per square inch of dummy area. The work done in inch-pounds per cubic inch of material, therefore, per inch of stroke is P , which is always larger than

$i \log_e \frac{A}{a}$ by the force necessary to force the dummy through the plastic material and to overcome adhesive resistance of the walls of the container on the billet and to overcome die friction.

Ordinary brass weighs 0.305 lb. per cu. in. Therefore, the work done within the material per pound of brass in foot-pounds is $\frac{i}{0.305 \times 12} \times \log_e \frac{A}{a}$. This equals $0.274 i \log_e \frac{A}{a}$. The specific heat of brass is approximately 0.095, and the heat equivalent of work is, therefore, 778 ft.-lb. $\times 0.095$, or 74 ft.-lb. Therefore 74 ft.-lb. is required to raise the temperature within the deformed material 1°F., or 133 ft.-lb. per 1°C. Therefore, the work done within the material in extrusion of brass will result in the temperature rise equal to

$$0.0036 i \log_e \frac{A}{a} \text{ per deg. F.}$$

$$\text{or } 0.002 i \log_e \frac{A}{a} \text{ per deg. C.}$$

Let I represent the minimum pressure per square inch of dummy area during the extrusion. ($I = P$ min.) In the extrusion of ordinary brass, $\frac{I}{\log_e \frac{A}{a}}$ usually will

increase with the copper content from 7000 to 10,000 lb. in alloys containing less than 61 per cent copper, as high as 16,000 to 22,000 lb. in alloys containing upward of 70 per cent copper, depending upon the temperature and rate of extrusion.

Table 1 has been compiled to show temperature rise with various ratios of

$\frac{A}{a}$ and with values of i given at 5000 lb., 10,000 lb., and 20,000 lb. per square inch:

Not all of this temperature rise is manifest in the extruded rod under ordinary speeds of extrusion. Some of it is expended in heat transfer to the die and back into the unextruded portion of the billet adjacent to the die, depending somewhat upon the rate of heat conductivity of the material and the rate of extrusion. But it is evident from this table that there is a limit in the extrusion of hard alloys to the

ratio of $\frac{A}{a}$ that is permissible because, on the one hand, there is a maximum permissible temperature of extrusion, which, if too near the melting point of the alloy, will allow insufficient leeway for temperature rise in the extrusion operation before incipient melting or cracking of the extruded section takes place. On the other hand, too low a temperature requires too high an initial extrusion pressure.

The pressure on the dummy required to extrude increases rapidly when the billet length is greater than its diameter. This is caused by the increased frictional effect of the container surface on the surface of the billet, which increases with billet length in resisting plastic flow due to surface adhesion and cooling. The pressure again increases, particularly with slow ratio of extrusion, as extrusion shortens the billet to 5 or 10 per cent of its original length, owing to temperature loss to container, die and dummy, and to the increasing effect of die and dummy end friction on the plastic flow. Further extrusion of this short end or stump only creates scrap, and is of no practical benefit.

Starting pressure has been found to be less by reverse extrusion. In the practice of reverse extrusion, the billet is introduced into the container, which, during extrusion, has the end nearest the pressure plunger closed. The die is fastened to a hollow ram inserted in the other end of the container.

TABLE 1.—Temperature Rises

$\frac{A}{a}$	$\log_e \frac{A}{a}$	i 5,000 Lb.	i 10,000 Lb.	i 20,000 Lb.
		°C.	°C.	°C.
8	2	20	40	80
20	3	30	60	120
56	4	40	80	160
90	4.5	45	90	180

The container and billet are then moved by the main ram over and against the die. The only movement of the plastic material during extrusion is at the die. As there is no

0.25 per cent) at billet temperatures from 750° to 770°C., is found to vary from 7500 to 10,000 lb. per sq. in. For cartridge brass (containing 68 to 71 per cent copper

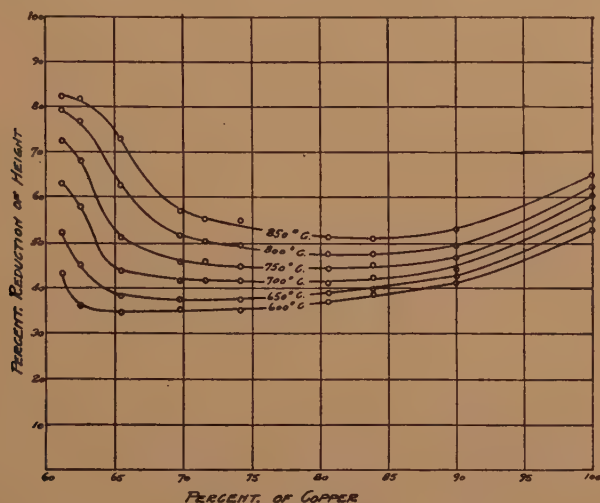


FIG. 2.—PLASTICITY OF COPPER-ZINC ALLOYS INDICATED BY DROP-HAMMER TEST ON HEATED SAMPLES. (Morris.²)

relative displacement of the unextruded portion of the billet with the container surrounding it during extrusion, the increased pressure involved in direct extrusion due to the effect of billet length is eliminated. In following this practice, however, it is difficult to obtain extruded material free from surface blisters and defects, owing to some of the oxidized surface of the billet being drawn into the die near the surface of the extruded section during extrusion. For this reason reverse extrusion has been little practiced commercially in this country.

In checking billet temperatures and ram pressures under normal extrusion rates with preheated containers and preheated tools, the basic pressure $\frac{I}{\log_e \frac{A}{a}}$ for the standard

free-turning brass-rod mixture (containing 60 to 61.5 per cent copper, 3.25 to 3.75 per cent lead, and the balance zinc, with some iron and tin impurity kept below

and balance zinc) extruded at 810° to 825°C., $\frac{I}{\log_e \frac{A}{a}}$ varies from 16,000 to 19,000

lb. per sq. in. of dummy area. In the former case, ram speeds run from 0.7 to 1.5 in. per sec.; in the latter, ram speeds are from 0.3 to 0.45 in. per second.

Comparison with Hot Hammer Tests

It is interesting to compare these pressures with those calculated from hot hammer tests by Dr. Alan Morris in 1931.² In Fig. 2 (Fig. 1 of Dr. Morris' paper) are plotted curves showing the percentages of deformation of heated slugs 0.5 in. in diameter by 0.750 in. long, of various copper alloys at different temperatures, to a 200-ft.-lb. blow delivered by a 50-lb. hammer dropping 4 ft. Fig. 3 (Fig. 3 of Dr. Morris' paper) shows the calculated resistance of the slugs in pounds per square inch of final slug area to blows at different percentages of reduction in

slug height. This resistance is shown to increase at any given temperature, with a copper content increasing from 61 to 71 per cent copper, and to remain fairly

operation, mostly on a 2200 to 2750-ton tube press used to extrude rod.

As it is necessary to throttle connections to gauges in order to protect the Bourdon

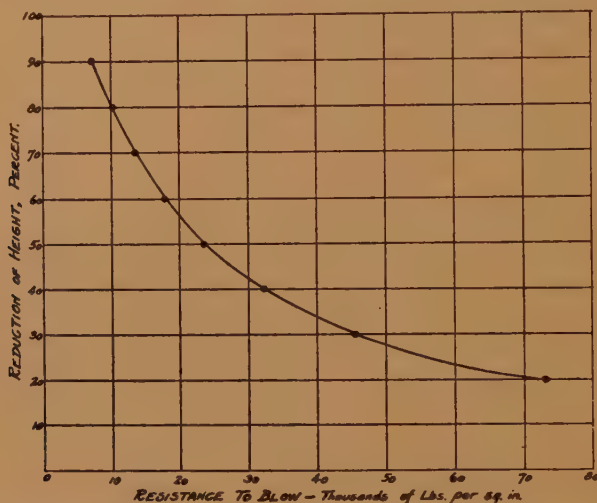


FIG. 3.—RELATION BETWEEN RESISTANCE TO BLOW AND REDUCTION OF HEIGHT. (Morris.²)

constant with increases in copper content up to 90 per cent. From 90 per cent to pure copper it reduces somewhat. These curves indicate a resistance of 12,500 lb. per sq. in. with 61 per cent copper at 750°C., as compared with the extrusion resistance *I* of 7500 to 10,000 lb. For 70 per cent copper, the hot hammer test shows an indicated resistance at 825°C. of 22,500 lb. per sq. in., while *I*, in extrusion tests, shows 16,000 to 18,000 lb. at the same temperature. These resistances to deformation are far greater than those shown by slow tensile tests on heated alloys. The comparison of extrusion resistance with hot hammer tests is made to indicate a similarity of results, and it is believed that very rapid rates of extrusion would require pressures approaching those shown by the hot hammer test (hot-hammer results influenced by end friction).

Average Results

Table 2 gives the average results of a number of tests made during commercial

tubes, the pressures recorded may be subject to slight error, but there are so many other uncontrollable variables in the operation, such as variable length of time between the withdrawal of the billet from the furnace and the application of pressure in the extrusion container, variation in copper content, variation in container temperature, die temperature, and dummy temperature, we cannot expect to obtain very close uniformity in readings taken from successive extrusions. The pressures recorded vary as much as 10 per cent above or below the average given in the table, and when it is noted that 25° variation in temperature in cartridge brass would result in 10 per cent apparent resistance to deformation, this is not surprising.

In screw-machine rod, variation in copper content of 1.5 per cent will show about 10 per cent variation in resistance at a given temperature.

In the most modern machines, the extrusion speed is controlled by two means, the main operating valve and an

adjustable throttle valve, which can be set to roughly control the extrusion speed desired. Under ordinary commercial practice, it is necessary to complete extrusion

predetermined opening, and opens the main valve wide when extrusion starts. If the billet is a little warmer than average, or its copper content a little lower than

TABLE 2.—Rod-extrusion Data Calculated from Gauge Readings^a
2200 TO 2750-TON EXTRUDER

	Nominal ^b			Temperature, Deg. C. ^d	Dummy Dia., In.	Rod Dia., In.	Ratio $\left(\frac{D}{d}\right)^2$	Log. R	Billet Length, In.	$\frac{L}{D}$	Maximum Pressure, Sq. In., Dummy	Minimum Pressure, Sq. In., Dummy	Maximum Pressure	Minimum Pressure	Extrusion Speed, In. per Sec.
	Cu	Zn													
Average mixture	69	31		825	9.38	2.81	11	2.4	28	3	55,000	38,000	23,000	16,000	0.4
	69	31		810	9.38	2.81	11	2.4	28	3	59,000	39,500	24,400	16,400	0.4
	69	31		820	9.38	2.81	11	2.4	18	2	49,000	38,000	20,500	16,000	0.4
	69	31		820	9.38	2@1.24	29	3.3	18	2	61,000	55,000	18,500	16,700	0.4
	69	31		810	8.25	0.800	97	4.5	14	1.75	100,000	84,000	22,400	18,700	0.3
3500-ton press	69	31		770	10.4	2@1.24	34	3.5	22	2.2	76,000	65,000	22,000	19,000	0.4
	Nominal ^{b,c}														
	Cu	Zn	Pb												
	61	35.5	3.5	750	9.38	2.65	14.3	2.65	28	3	43,000	26,500	16,000	10,000	1.0 Av.
	61	35.5	3.5	705	9.38	2.65	14.3	2.65	18	2	34,000	24,000	12,700	9,100	1.5 Av.
	61	35.5	3.5	705	9.38	1.1	83	4.4	28	3	42,500	35,000	9,500	8,000	0.8 Av.
	61	35.5	3.5	705	9.38	1.1	83	4.4	18	2	40,500	33,500	9,200	7,500	0.7 Av.

^a Owing to throttle effect of gauge piping, readings are subject to some error if pressures change rapidly.

^b Copper and zinc may vary ± 1 per cent.

^c Lead may vary ± 0.25 per cent.

^d Temperatures vary $\pm 10^\circ$.

^e Pressures vary ± 10 per cent.

TABLE 3.—Tube-extrusion Data Calculated from Pressure Readings^a
2000 TO 2200-TON HORIZONTAL TUBE EXTRUDER

Metal	Nominal Mixture ^b			Temperature, ^c Deg. C.	Dummy Dia. D, In.	Tube Dia., In.	Mandrel Dia., In.	Tube Area ^a	Ratio $\frac{\pi D^2}{4a}$ R	Log. R	Billet Length, In.	Maximum Pres- sure, Lb. per Sq. In., Dummy	Minimum Pres- sure, Lb. per Sq. In., Dummy	Maximum Pres- sure, Log. R	Minimum Pres- sure, Log. R	Extrusion Speed, ^e In. per Sec.
	Cu	Zn	Sn Pb													
Admiralty..	70	29.0	1.0	800	8.11	2 $\frac{3}{16}$	2 $\frac{1}{16}$	2.85	19	2.95	13.5	66,000	58,000	22,500	19,700	0.7
Alpha.....	67	32.5	0.5	740	8.11	3 $\frac{1}{16}$	2 $\frac{1}{16}$	3.9	13.3	2.6	9	58,000	48,000	22,200	17,700	1.4
Leaded 2 and 1....	67	31.5	1.5	720 \pm	8.11	3 $\frac{1}{2}$	2 $\frac{7}{16}$	4.8	11	2.4	10.5	63,000	48,000	26,000	20,000	1.2
Aluminum brass....	77	21.0	2.0	835	8.11	2 $\frac{1}{2}$	1 $\frac{7}{8}$	2.14	24.4	3.2	8.75	69,000	56,500	21,600	17,700	0.9

^a This tabulation represents average results from 20 readings of each alloy.

^b Copper content may vary ± 1 per cent.

^c Temperatures varied $\pm 10^\circ$.

^d Pressures varied ± 10 per cent.

^e Speeds varied ± 20 per cent.

with sufficient rapidity to prevent excessive temperature drop in the billet through transfer of heat to dummy, container liner, and die face from unduly increasing the resistance to extrusion. Quite frequently the operator sets the throttle valve at a

average, extrusion will take place more rapidly until there is a balance between increasing pressure required with increasing extrusion speed and the pressure drop due to speed of flow through the throttle valve to the main plunger. The ex-

perienced operator can soon determine the best billet temperature and speed of extrusion for any given billet analysis, length, and die area, and will vary these

in rods. This tube extrusion shows a slightly higher minimum extrusion pressure than is shown in the average rod extrusion, and a somewhat lower maximum, the latter

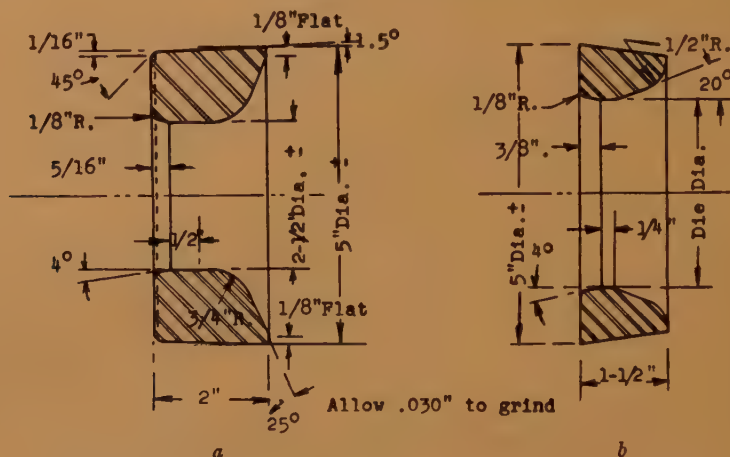


FIG. 4.—EXTRUSION DIES, COPPER-BASE ALLOY: (a) TUBE, (b) ROD.

Analysis: C, 0.50 per cent; Cr, 4.00; Va, 1.00; W, 18.

Heat-treatment: Preheat, 1600°F.; high heat, 2250°F.; quench, oil and air; draw, 1260° to 1340°F.; hardness, Rockwell C-34 to C-43.

somewhat, depending upon whether he is starting up in the morning with a cold container liner or running under normal operating conditions.

Multiple-hole extrusion is resorted to where the $\left(\frac{D}{d}\right)^2$ and $\frac{L}{D}$ are too large to permit of successful extrusion of a single small section. The pressure required in multiple extrusion is somewhat greater than with a single hole of area equal to those of the multiple dies, owing to greater surface areas of the multiple dies, but not in proportion to the benefit derived from the reduction of pressure caused by reducing $\log. \left(\frac{D}{d}\right)^2$ to $\log. \left(\frac{D}{2d}\right)^2$ or $\log. \left(\frac{D}{3d}\right)^2$.

Table 3 gives data obtained from the tube extrusion of four different alloys. Only one of these alloys can be directly compared with the rod-extrusion data given in Table 2. The admiralty metal has resistance to hot-working comparable to the 69-31 copper-zinc mixture as used

because the billet length is less in all cases than in rod extrusion.

It is to be expected that the basic pressure in tube extrusion would be slightly higher because of the increase in chilling of the billet by the piercing mandrel and the increased frictional resistance caused by the mandrel surface during extrusion.

Also, the speeds were somewhat greater in the tube extrusion than in that of the rod. It is desirable to extrude tubing at a considerably faster rate than rod in order to keep the contact time between the piercing mandrel and the billet within as short a period of time as possible, so that the mandrel will not be heated sufficiently to unduly reduce its tensile strength.

The piercing mandrels usually are made from chrome-tungsten or chrome-tungsten-molybdenum steel with the two latter elements kept sufficiently low to prevent cracking when water is applied for cooling between extrusions. When alloys require higher extrusion temperatures or longer

contact with the heated billet, it may be necessary to use mandrels with higher tungsten and chrome content, and then oil cooling may be necessary between extrusions. This is particularly true in vertical extrusion in which small billets and small-diameter mandrels, say from 1 to 1½ in., are used in the extrusion of small-size tubing.

TOOLS

In the early days of extrusion, the grades of steel available for tools interposed a definite limit to the copper content of the brass alloys that could be extruded, and the operation was confined to the Muntz metal group containing from 56 to 61 per cent copper. As alloy steels were developed and heat-treatments perfected, it became possible to extrude alloys having a greater resistance to hot-working, until today it is possible to utilize pressures in extrusion of more than 100,000 lb. per sq. in. of ram pressure. With the harder alloys, much greater care must be taken in the entire operation. Hot-working tools suitable for handling higher temperatures and pressures are subject to cracking if local stresses of too great magnitude are introduced by sudden application of heat when in the cold state, or too rapid chilling when hot. Therefore, these tools must be slowly preheated and maintained at a

suitable temperature at all times during their use. Preheating also limits the amount of heat absorbed from the billet and prevents lowering its temperature during extrusion to the point where the pressure of the main ram is insufficient to complete the operation.

Fig. 4 shows standard shapes, analysis, and heat-treatment that have been used successfully in extruding brass rod and tubes.

ACKNOWLEDGMENT

The authors wish to thank Dr. Alan Morris, Mr. Harold Blomquist, Mr. Theodore Carlson, and other members of the Research and Metallurgical Department at the Bridgeport Brass Co., for supplying test data from which Tables 2 and 3 were prepared.

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DISCUSSION

See page 466.

Some Factors Affecting the Rate of Extrusion of Aluminum Alloys

By T. L. FRITZLEN*

EXTRUSION of aluminum alloys in this country is performed mainly by direct extrusion, therefore this paper is confined only to factors affecting the rate of extrusion by this method.

Many factors affect the rate of extrusion of aluminum alloys. It is the purpose of this paper to present a discussion on the factors that are subject to technical control. Most of them are closely related, so that a clear-cut distinction between them is rather difficult. However, an attempt will be made to evaluate the effect of each factor separately, as far as possible. The most important factors only will be considered, and these will be discussed in detail under three general headings: (1) characteristics of the equipment, (2) size and structure of the ingot, and (3) temperature of ingot, cylinder, and other parts.

It is a well established fact¹ that the pressure and the speed of extrusion are related and are exponential functions of one another. Therefore, whenever a certain condition tends, for instance, to increase the pressure required for extrusion, it will reduce the extrusion speed if the pressure is maintained constant. For this reason, in this paper the effect of various conditions is expressed either in regard to their effect on the pressure required or the extrusion speed.

Another established fact is the relation-

ship between the temperature of the material being extruded and the pressure required to extrude. According to Schishokin,² this relationship is of the exponential type, and as the temperature is increased the pressure required is decreased.

It would seem from the preceding that the greatest rates of extrusion can be obtained by the use of higher temperatures. However, as is well known, other factors intervene to limit the rate of extrusion of aluminum alloys when increasing the temperature. These factors will be discussed in detail later.

CHARACTERISTICS OF THE EQUIPMENT

The capacity of the press determines the maximum unitary pressure that can be applied for any given cylinder diameter. Pressures used for extrusion of aluminum alloys range from approximately 50,000 lb. per sq. in. to 150,000 lb. per sq. in., dependent upon the alloy and the size of the shape extruded. Higher pressures could be used to advantage, but existing steels limit pressures employed in the production of extrusions.

Numerous mechanical characteristics of the extrusion press affect extrusion rate. The most important characteristics of the press itself are: (1) sensitivity of the main pressure valve and accuracy of pressure gauges, (2) accuracy of equipment to heat the cylinder uniformly and to control cylinder temperature, and (3) accuracy of means of measuring the speed of extrusion. The variables subject to control during the extrusion operation are pressure, temperature, and speed, and it is evident that the preceding characteristics

Manuscript received at the office of the Institute December 27, 1944. Listed for New York Meeting, February 1945, which was canceled. Issued as T.P. 1851 in METALS TECHNOLOGY, October 1945.

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¹ References are at the end of the paper.

of the press should be such as to enable close control of these variables.

The strength of the auxiliary equipment, such as tool holder, die, back-up piece and block, may limit the maximum pressure that can be exerted during extrusion. For example, a die with a long tongue cannot stand as much pressure as a die with a short tongue.

The length, contour and size of the extrusion die also affect the rate of production. The shorter the length of the die bearing, the lower the pressure required to extrude. This fact, well known to makers of extrusion dies, is used when irregular shapes, with thin and thick parts, are to be extruded. In a shape with wide variations of thickness the thicker parts tend to flow faster, producing warping, and, in extreme cases, breaking of the thinner sections. By lengthening the die in the place of the thicker sections, the flow is slowed down in these zones so as to get a more even movement of the metal through the die.

Another factor affecting the extrusion speed is the sharpness of corners or fillets in the extruded shape. Cracks or checks, produced by too high a speed of extrusion, always start at the sharp corners, so that the speed must be limited for shapes with sharp corners. Consequently, it is advantageous to employ as liberal radii as possible for aluminum-alloy shapes, particularly for the stronger alloys.

The size of the die opening also affects the rate of production. The friction between the metal and the die is higher the smaller the cross-sectional area of the shape, creating the need for higher pressures for thin material. The flow of the metal also is easier in shapes with large cross-sectional areas, because the internal friction of the metal is lower and consequently the pressure required is lower.

The area of the cylinder divided by the area of the orifice or orifices in the die gives the reduction of area from ingot to

extruded shapes, which is termed extrusion ratio. It is evident that the larger the area of the orifices in the die, the easier it is to press the material through the die, therefore the lower the pressure required to extrude the material.

For this reason the extrusion ratio should be kept as low as possible. For a determined shape this can be accomplished in two ways: either by reducing the size of the ingot to be extruded, or by using a multiple die from which several shapes are extruded at the same time.

A reduction of the size of the ingot is not conducive to high production rates, since less material is extruded by one stroke and the time spent reloading the press for the next extrusion is many times more than the time that can be gained by speeding up the extrusion in this way. In a normal cycle of production, roughly as much time is spent preparing the press for extrusion as is required for the actual extrusion. A gain in the extrusion speed obtained by reducing the extrusion ratio through a reduction of the size of the ingot would produce a loss of production.

There are limitations also to the use of multiple dies. The handling of too many shapes extruded at the same time from one ingot is difficult, and defects are likely to appear in the product. The maximum number of extrusions that can be handled economically varies with the shape and size of the product. Usually this limit ranges from two for complex shapes to eight or ten for small simple extrusions.

Another factor that limits reduction of the extrusion ratio is the structure of the material. If the extrusion ratio is very low, say 2 to 3, the as-cast structure is not broken up completely and the mechanical properties of the material are likely to be below minimum. This factor is not very important if the extruded product is to be further worked, but when the product is to be used as extruded, or finished to size by drawing, extrusion

ratios below 5 or 6 cannot be used. Figs. 1 and 2 show the effect of the ratio of extrusion on the microstructure.

of a 2500-ton press in the extrusion of strong alloys, the cylinder size and consequent diameter of ingot should be selected

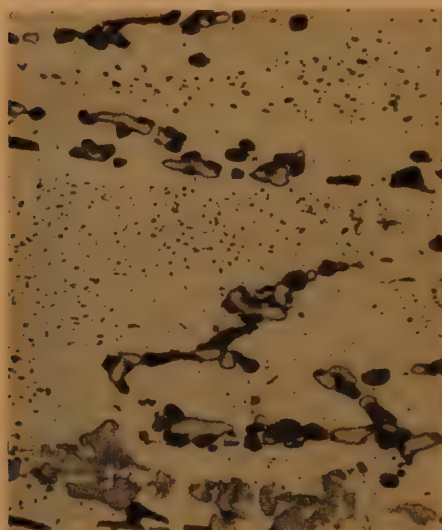


FIG. 1.
FIG. 1.—24 S INGOT EXTRUDED WITH A RATIO 3. UNETCHED. $\times 500$.
As-cast structure not broken, only partially elongated.



FIG. 2.
FIG. 2.—24 S INGOT EXTRUDED WITH A RATIO 10. UNETCHED. $\times 500$.
As-cast structure completely broken.

SIZE AND STRUCTURE OF THE INGOT

As previously mentioned, the capacity of the press determines the maximum pressure that can be applied for any given cylinder diameter.

The unitary pressure exerted on the ingot is the main factor governing the rate of extrusion. It is evident that the size of the ingot is governed by the capacity of the press.

In technical control of extrusion we are interested in utilizing the press capacity efficiently within practical limits, and this determines the diameter of ingot to be used. A $6\frac{1}{2}$ in. cylinder in a 2500-ton press will allow the application of 150,000 lb. per sq. in. on the aluminum-alloy ingot contained therein, while an 8-in. cylinder in the same press will allow the application of 100,000 lb. per sq. in. Therefore, for the most efficient utilization

to extrude at pressures as close to 150,000 lb. per sq. in. as possible. However, for softer alloys, a 2500-ton press can be used with larger cylinders, because the pressure required to extrude these alloys is lower.

The length of the ingot to be extruded should also be considered. With the longer ingot the surface in contact with the cylinder increases and correspondingly the friction increases. As an example, doubling the length of an ingot of 14S, 17S, and 24S when extruding any particular shape will increase the pressure required approximately 15 to 20 per cent, and will decrease the allowable extrusion speed as much as 50 to 75 per cent, if other factors remain unchanged.

However, in production, the higher pressure required for the longer ingots results in lower extrusion speed, owing to the required use of higher temperature;

that is, if extrusion is being performed employing minimum temperature and maximum press capacity, in order to obtain the highest speed. Since the length of the ingot to extrude affects pressure, temperature, and speed to such an extent, it will be discussed in detail.

The length of section or shape to be extruded should be limited to 60 ft., or shorter, as it has been observed that this generally allows extrusions to be produced at the highest speed with the best surface. Other considerations determining the length are the handling methods, the finished length, the maximum rough length that can be heat-treated, and the amount of butt end or discard.

The charging of the ingot in the cylinder, the charging of the dummy or follow-block, the movement of the press ram forward, the building up of pressure required for extrusion, the slackening off of pressure, the running out of tools, the movement of the ram, and the shearing off of the part of the ingot not extruded (termed butt end) requires time other than that required for actually pushing the shape through the die. This time will be referred to as the loading time, and for a 6½-in. cylinder in a 2500-ton press will amount to approximately 2 min. This idle time must be taken into consideration when determining the most efficient ingot length to use; for example, the following case:

1. Shape having area of 0.165 sq. in. is to be extruded through a four-hole die.
2. Ingot diameter to be used, 6.25 inches.
3. Finished length, 12 ft per piece.

The following comparison is between the production to be obtained when extruding ingots under the conditions described, to obtain two finished lengths per hole and four finished lengths per hole. The number of finished pieces produced from one charge will be 8, and in the second will be 16.

In both cases the extrusion ratio (ratio

of ingot cross-sectional area to area of shapes extruded) would be: ingot diameter 6.25 in., area 30.66 sq. in.; four shapes having 0.165 sq. in. area equal to 0.660 sq. in. $\frac{30.66}{0.660} = 46$ ratio of extrusion.

Two Pieces per Hole

To obtain two finished lengths of 12 ft. each, it is necessary to extrude approximately 26 feet.

This extruded length, 26 ft., divided by the extrusion ratio, 46, gives the length of ingot required (0.57 or 0.6 ft.). The length of ingot required is then 7 in. plus a 10 per cent allowance for butt end or discard, which makes the total length 8 inches.

Assuming that an 8-in. long ingot will allow extrusion at 16 ft. per min., the extrusion time required to extrude the 26-ft. length will be $2\frac{5}{6} = 1.63$ minutes.

This time, added to the loading time of 2 min., gives the total time required for one cycle as 3.63 min. The number of cycles in one hour will therefore be $60/3.63 = 16.5$ cycles per hour. The number of finished lengths produced per cycle is 2, so that the total of pieces produced in one hour will be $8 \times 16.5 = 132$ pieces.

Four Pieces per Hole

To obtain four finished lengths of 12 ft. each, it is necessary to extrude approximately 52 ft., and 52 ft. divided by the extrusion ratio, 46, gives the length of ingot required as 14 in. With the addition of 10 per cent for butt discard, this length becomes 15.5 in., or, in round figures, 16 in. The extrusion speed for this ingot will be approximately 8 ft. per min., so that extrusion time will be $5\frac{1}{2} = 6.5$ minutes.

Adding the 2 min. loading time, the total time will be 8.5 min. per cycle, $60/8.5 = 7$ cycles per hour. The number of finished lengths produced per cycle

is 16, so that the total production per hour is $16 \times 7 = 112$ pieces.

Therefore, in this particular case, the use of the shorter ingot would result in approximately 17 per cent more press production as compared with that produced from the longer ingot. In other cases, however, it may be more efficient to use the longer ingot. The only way to determine which is the most efficient is to try both the short and long ingot whenever there is a question; although, through experience, it can be judged rather closely.

The alloy composition is also an important factor in the extrusion rate. The various aluminum alloys require different pressures to extrude; those alloys requiring the least pressure can be extruded at the highest speeds.

The common aluminum alloys, listed in order of required pressure of extrusion, from the lowest to the highest, are:

2S
3S
53S, 61S
52S, 25S
14S, 17S, 11S
24S, 18S, 56S
75S, R303

The more pressure an alloy requires for extrusion, the higher the temperature required, and subsequently the lower the allowable extrusion speed. The structure of the metal is also a very important factor governing the rate of extrusion.

Aluminum alloys in the as-cast condition tend to show a cored structure, as shown in Fig. 3. This tendency, which is practically absent in alloys with low content of alloying elements, like 2S or 3S, is very pronounced in alloys with high copper or magnesium contents, as 24S or 56S. The network visible in this figure has a higher copper content than the average and therefore is harder than the normal alloy when homogeneous. Naturally, this hard network

will require higher pressure of extrusion than normal. For this reason the extrusion of as-cast ingots must be conducted at lower speeds than ingots having homogeneous structure. By controlling the casting procedure, it is possible to reduce this coring effect; however, the control required is so close as to make it impossible in normal conditions of production. To minimize this lack of homogeneity of the material, a solution treatment of the ingot is necessary.³

The temperature to be used is determined by the alloy, and it is the highest that can be used without producing eutectic melting in the alloy. The time of the soaking is governed by the type of ingot, size, and alloy, and ranges from 2 hr. for small ingots up to 20 to 24 hr. for large ingots of alloys with high magnesium content. Even after such a long period the structure of the material is not completely homogenized, as shown by Fig. 4, but the remaining segregation is so reduced as to make a longer soaking uneconomical.

For high-strength aluminum alloys, it has been found⁴ that a slow cooling after homogenization permits lower pressures to be employed. The slow cooling permits dissolved constituents to precipitate out of solution so that the ingot is in the annealed state, rather than in the solution-treated state. Naturally, this slow cooling can be employed advantageously only when the temperature at which an ingot is reheated for extrusion is not so high as to produce appreciable solution of constituents.

Temperature

The temperature of the material being extruded and the temperature of the equipment are very important factors governing the rate of extrusion. When extruding, stresses are set up in the shape at the point where it emerges from the die. The higher the extrusion pressure, the higher these stresses. If these stresses

exceed the strength of the shape, breakage will occur. The strength of aluminum alloys, as of all other materials, decreases with increasing temperatures. This de-

For these reasons, the speed of extrusion is dependent upon the temperature, not only as a function of the pressure that will generate stresses, but also as to the

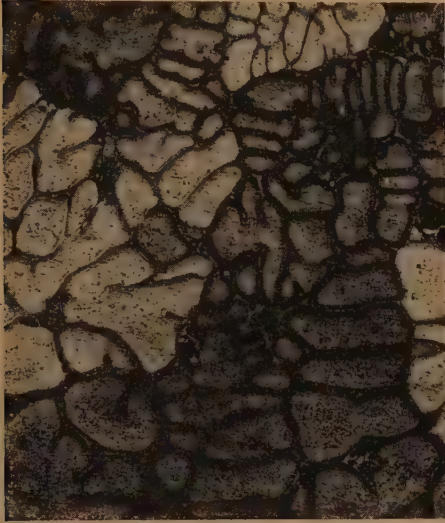


FIG. 3.

FIG. 3.—AS-CAST STRUCTURE OF A 14S INGOT. ETCHED WITH KELLER'S ETCH. $\times 75$. Notice darker color of dendritic network, resulting from higher copper content.



FIG. 4.

FIG. 4.—HOMOGENIZED STRUCTURE OF A 14S INGOT. ETCHED WITH KELLER'S ETCH. $\times 75$.

Notice almost complete disappearance of color difference of dendritic network, showing that the Cu content has been equalized by the homogenizing treatment.

crease is particularly appreciable at the temperatures used for extrusion.

A large part of the work produced by the extrusion is transformed in heat,⁵ most of which is dissipated to the air, either directly from the shape or through the cylinder and die. When the rate at which this heat is generated surpasses the rate of dispersion, the temperature of the shape will rise. Under conditions normally used the temperature of the shape emerging from the die increases as the extrusion progresses. This rise in temperature will further reduce the strength of the material, and in extreme cases may be of such a magnitude that the eutectic temperature of the alloy being extruded is reached. At this temperature the strength of the alloy drops abruptly.

amount of heat generated in the unit of time. Fig. 5 illustrates the effect of temperatures in the range between 600° and 900°F. on the pressure and the speed allowing extrusion of a commercial product. The speed shown in Fig. 5 represents the approximate maximum that can be used without producing breakage of the shape. The curve of the pressure shows the pressures required to obtain the speeds shown in the graph.

From this graph it is evident that decreases in temperature in the range of 600° to 725°F. have much more effect on the allowable speed for the aluminum alloys considered than have corresponding decreases of temperature above 725°F. On the contrary, the pressure is little affected at the lower temperatures con-

sidered, but decreases sharply at the higher temperatures.

A comparison of the curve representing the maximum allowable speed as shown in

as possible, the ingot will be at a high temperature at the start and will be cooled down gradually by the cylinder, which is at a lower temperature.

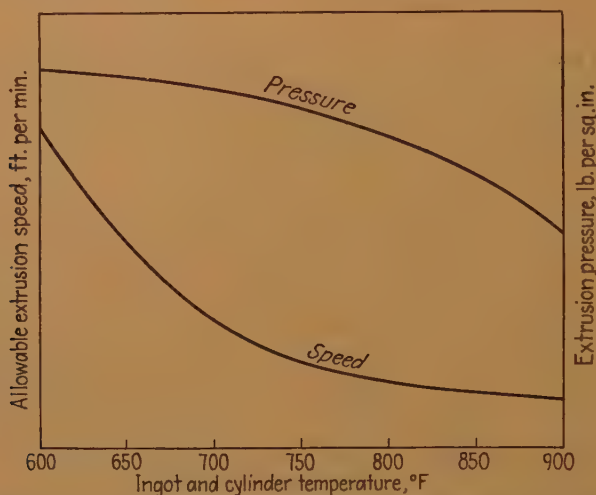


FIG. 5.—APPROXIMATE RELATION BETWEEN TEMPERATURE, PRESSURE, AND ALLOWABLE SPEED IN EXTRUSION OF 14S, 17S, AND 24S. OTHER FACTORS CONSTANT.

Fig. 5 with data^{6,7,8} on the mechanical properties of aluminum alloys at elevated temperatures shows a very close relationship. This relationship shows that the main factor governing the maximum allowable speed is the strength of the material when emerging from the die as pointed out previously.

As is well known, in direct extrusion the pressure is maximum at the start and then decreases with progression of extrusion.⁹ For minimum pressure requirement, the material should be as hot as possible at the start of extrusion. On the other hand, when extrusion has started, the pressure will drop and the important factor becomes the speed of extrusion. To obtain maximum speeds of extrusion, the temperature of the emerging shape should be as low as possible.

These contradictory requirements can be met by having the ingot at a higher temperature than the extrusion-press cylinder. If the extrusion is started as quickly

Actual production data have shown that the best results with strong aluminum alloys are obtained when this temperature difference is of the order of 50°F. In strong aluminum alloys increases of allowable speed from 25 to 60 per cent have been obtained when using this temperature difference, as compared with extrusions conducted with ingots at a temperature 100° to 200°F. lower than the cylinder temperature.

In the latter case maximum pressure is required to start extrusion and there is a marked drop in required pressure when the charge is started. In the first case maximum pressure is also required at the start, but the pressure drop is not as great because of the cooling of the ingot by the cylinder.

The large mass of the press cylinder in relation to the mass of the ingot causes the cylinder to have a pronounced effect on the temperature of the emerging shape. A cylinder at a temperature lower than the

starting ingot temperature will extract heat from the ingot as extrusion progresses. This enables extrusion at a higher speed, since it lowers the temperature of the emerging shape and tends to counteract the normal increase in temperature obtained in the shape as extrusion progresses. Since the temperature of the shape limits the allowable stresses, and these stresses are dependent upon the pressure and therefore govern the speed of extrusion, it is evident that a close control of the temperature of the cylinder is an important factor.

The most important zone of the cylinder in regard to temperature of the shape is the die end. Especially close control in this zone is very important.

Die, back-up and block temperatures also are important, especially when extruding shapes less than 0.064 in. thick, since the thinner shapes cool more rapidly than the heavier shapes when passing through the die.

Attempts have been made^{10,11} to cool the die either during extrusion or between cycles. This would permit the use of high temperatures of the ingot, which are conducive to higher speeds, and at the same time would keep the temperature of the emerging shape low enough to obtain in the shape sufficient strength to withstand the higher stresses produced by the higher speeds.

Numerous other factors affect the rate of extrusion, such as condition of the die, mechanical troubles, tolerance allowed and cleanliness of the metal, but the factors covered in this paper have proved to be the most important ones and those requiring close control to obtain maximum production.

SUMMARY

The most important factors governing the rate of extrusion of aluminum alloys were discussed:

1. The characteristics of the extrusion press and auxiliary equipment are limiting factors in production.

2. The ingot size and structure affect the rate of extrusion—longer ingots require greater pressures. Higher extrusion ratios require greater pressure. The stronger alloys require lower pressure in the homogenized condition than in the as-cast state.

3. The temperature of the ingot and cylinder and their relationship affect the rate of extrusion to a marked extent.

The main factor governing the maximum allowable speed is the strength of the shape at the time it emerges from the die. This strength is dependent upon the temperature of the shape at this point in the operation.

ACKNOWLEDGMENTS

The author wishes to make acknowledgment to the Reynolds Metals Co. for the permission to present this paper, and to all those in the Reynolds Metals Co. who have cooperated in this work.

Special acknowledgment is due Mr. I. P. Macauley, Mr. C. F. Tichy, Mr. H. D. Bitner, Mr. T. D. Stay, Mr. H. E. Logsdon and Dr. L. F. Mondolfo for their assistance in the compilation of this paper.

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DISCUSSION

(A. B. Cudebec presiding)

This discussion refers also to the paper by W. W. Cotter and W. R. Clark, pp. 447 to 457.

W. R. CLARK.—The subject mentioned is rather a broad subject and when Major Cudebec asked us to prepare a paper, we were not familiar with the fact that Mr. Pearson, in England, had just published or was in the process of publishing quite an extensive treatise on the subject of extrusion, which covered the entire field.

We were, therefore, more or less at a loss to know what to prepare, and of necessity we confined ourselves to the copper and brass problems, such as we had encountered in our own factory in extruding the well-known alloys and in attempting to extrude some of the lesser known alloys in attempts to develop better and stronger materials.

THE CHAIRMAN.—We now have the pleasure of a paper presented by Mr. T. L. Fritzlen.

T. L. FRITZLEN.—I would like to preface the presentation of this paper by a few remarks on the extrusion process in general.

Extrusion of aluminum alloys for a considerable number of years was more in the nature of an art than of a science. This paper evaluates the extrusion factors, particularly applicable to the stronger alloys of aluminum, with respect to technical control.

In other words, an attempt has been made to remove extrusion from an art to a science. However, extrusion of aluminum shapes is somewhat of a jobbing operation, and there are so many factors that affect the extrusion of any one section with relation to the alloy that the paper is somewhat general. For example, the extrusion of a plain angle with equal legs and equal thickness differs considerably from an angle of the same thickness with legs of unequal length, or from an angle that has one leg of one thickness and another leg of a different thickness.

THE CHAIRMAN.—Two short films of extrusion methods will now be shown; the first

one of the copper-brass industry, and the second of the aluminum industry.

(The films were shown)

Now we have about an hour of Panel Board discussion. As the Panel Board members, we have: Mr. W. W. Cotter, from the Bridgeport Brass Co., Bridgeport, Conn.; Mr. R. W. Andrews, Jr., of the Aluminum Company of America, Pittsburgh, Pa.; Mr. A. W. Winston, of the Dow Chemical Co., Midland, Mich., and Mr. G. M. Bouton, of the Bell Telephone Laboratories, New York.

C. H. LORIG.*—I have a number of questions that I would like to ask Mr. Winston. One is: To what extent has magnesium extrusion been developed? Is it now available for general use or is it still limited to the specific purposes? What is the outlook for the future?

A. W. WINSTON.—Referring to the first question, it may be said that magnesium alloys are being extruded regularly in commercial production, and are available in a wide variety of shapes for general use.

The extrusion of magnesium sections began in 1930 in this country, but they did not become well known until the latter part of the decade. With the development of the war program, several fabricators came into the field, and at this time there are at least four who are competent in the field of magnesium extrusion. During the war, very considerable quantities of extruded magnesium structural shapes were used successfully in military aircraft.

An adequate number of magnesium alloys is available, and it is possible to extrude these alloys in a practically unlimited variety of shapes, as may be required for specific applications. The largest structural section made up to the present is a 10-in. I-beam, extruded in a 5500-ton press from a billet that is 12 in. in diameter. Billets as large as 16 in. in diameter have been used in the production of large bars and slabs.

As they possess very favorable strength-weight ratios, extruded magnesium alloys undoubtedly will be chosen in the future for

* Battelle Memorial Institute, Columbus, Ohio.

many applications in which the maximum lightness is desired.

J. ALICO.*—Has any work been done with homogenized magnesium billets prior to extrusion? Does homogenization tend to improve a magnesium extruded shape or is it not necessary to go to that extent?

A. W. WINSTON.—Whether magnesium billets should be homogenized before extrusion will depend upon the alloy and type of billets being extruded.

If it is the alloy containing magnesium and 1.5 per cent manganese (Dowmetal M) homogenizing is of no value and extrusion may be started as soon as the billets are brought up to temperature.

With material containing a higher alloy content, such as the alloy containing 8.5 per cent aluminum and about 0.5 per cent zinc (Dowmetal O), homogenizing before extrusion is performed frequently. It depends to some extent upon the metallurgical structure of the billet.

Formerly, billets were made in heavy-walled cast-iron molds, and considerable segregation of magnesium-aluminum compound in large particle sizes was present. It was very necessary to homogenize billets of this type in order to secure the solution of the constituents and freedom from compound stringers in the extruded product.

At the present time, direct-chill continuously cast billets are used with very fine grain size, very small compound particle size and good distribution of the compound. It is no longer necessary for most applications to homogenize before extrusion.

W. R. CLARK.—Do the pressures and temperatures involved in extrusion of magnesium closely follow those of aluminum?

A. W. WINSTON.—The extrusion temperatures with magnesium vary somewhat with the alloy composition, but are in the range of from 600° to 800°F.

The pressures involved run from about 50,000 lb. per sq. in. unit pressure on the billet to as high as 150,000. In Mr. Fritzlen's paper, about the same pressure range is mentioned for aluminum alloys.

*Singmaster and Breyer, New York, New York.

The pressure, of course, will vary, depending upon the shape of the section being extruded, the lower pressures applying to heavy bars and rather low reductions. By that is meant a small reduction from the original billet area. The higher pressures will apply to thin sections that may be extruded with a much higher reduction or extrusion ratio. For magnesium, the ratio should be at least 10 to 1, and preferably 20 to 1.

Perhaps Mr. Andrews can supply comparable data for the aluminum alloys.

R. W. ANDREWS, JR.—Generally speaking, the temperatures for aluminum are approximately the same as those for magnesium as Mr. Winston has outlined them.

There is just one thing about this question of pressures that I like to think about. After all, an extrusion die is nothing but a fluid orifice, and if you remember your hydrodynamics, with a given head on one side and discharging to atmosphere on the other, the pressure required to maintain a certain speed or a certain quantity of flow is regulated by the character of the orifice itself.

So that, generally speaking, the only reason that we are interested in pressures is that we are limited by the maximum specific pressure we can apply to the ingot. I would like to point out a difference in nomenclature between aluminum and copper and brass, in which we choose to call the piece of metal that we put into the extrusion container an ingot, because it is cast and not previously worked.

T. L. FRITZLEN.—If magnesium tubing is made, which I assume it is, is it made by extruding a hollow ingot and subsequent drawing either hot or cold, or is it extruded from a solid ingot?

A. W. WINSTON.—Magnesium tubing can be made either by extruding a hollow or solid ingot or billet. It is possible to use solid billets and pierce them in the conventional way but this is not the usual method. Some tubing in the smaller sizes is made from bored billets in an extruder with a fixed mandrel on the stem. Most of the magnesium tubing produced today, however, is made from solid billets by the use of "spider" or "bridge" dies.

The tubing usually is extruded to size and is not subsequently drawn or otherwise pro-

cessed. Magnesium can be drawn but the reductions must be lighter than with other nonferrous metals, and more frequent annealing is necessary. It appears to be more economical, therefore, to extrude to size.

A. R. KAUFMANN.*—In the extrusion of magnesium do you sometimes encounter so-called rattlesnake or Christmas tree effects in the rods, like those in aluminum under improper extrusion conditions? Rings develop around the rod if a rod is being extruded, and finally it breaks up into short segments. Is the condition known to be related to the friction between the magnesium and the die, or the conditions of lubrication, or the temperature produced as determined by the rate of extrusion, or just what might be the conditions?

A. W. WINSTON.—The trouble sounds like exaggerated tensile hot-short cracking of the surface caused by extruding too fast at too high a temperature, with perhaps an incorrect entering radius or too long a land on the die. The center material tends to go faster than the outside surface in contact with the die, which exerts considerable frictional restraint. The die may need to be redesigned to balance the restraint over the entire cross section of shape.

The usual correction would be to reduce the speed and temperature and possibly adjust the die design. The trouble occurs once in a while with magnesium but, of course, is avoided as much as possible.

H. B. BURRACK.†—I would like to ask Mr. Andrews two questions:

1. Frequently statements are heard from people in the high-strength wrought-aluminum alloy field that when an as-cast ingot cannot be rolled because of its brittle qualities, it is possible to extrude it successfully; for instance, high-magnesium aluminum alloys can be extruded successfully although they are generally, from the practical standpoint, considered impossible to roll.

2. In the motion picture just presented by our company, no indication was given as to prospects of improving the corrosion

resistance of extruded shapes by means of cladding. Practically all of our sheet products, during the war, were clad so as to provide for the best possible corrosion resistance under service conditions. What are the prospects of cladding extrusions at present?

R. W. ANDREWS, JR.—I think I should preface my answer with a statement that I am a mechanical engineer and not a metallurgist. I have not the slightest idea of the metallurgical aspects (if there are any) of your question.

However, I think that frequently we draw conclusions from inconclusive evidence. I think that a great many times we say that things cannot be rolled because we do not attempt to roll them the right way, and we say they can be extruded because extrusion is a relatively simple, inexpensive means of producing a complicated shape.

Rather obviously, extrusion can do many things that rolling cannot do, for the reason that it is impossible to have reentrant corners in a rolled shape.

The very elements of shape rolling limit the type of shapes that can be used. If you noticed some of the exhibits outside—and we have some 50,000 or 60,000 different extruded shapes, which have been made over a period of years—nine tenths of those are produced because they are shapes that could not be rolled or because they are produced in quantities that are uneconomical to roll.

The extrusion process, generally speaking, is a very desirable process for many intricate shapes that would require very expensive tooling, very expensive roll costs.

When you are dealing entirely with structural shape—that is, conventional stuff out of the Steel Construction Institute Handbook—things that can be rolled in steel most certainly can be rolled in aluminum, so that leaving metallurgy out of the question for the moment, which I cannot answer, my own feeling is that the answer to your first question is a mechanical answer rather than a metallurgical one.

Your second question deals with cladding of extrusions. That is something that we would all like to see. It is something that is not commercially developed today.

I think that there has been a great deal of very satisfactory experience with the clad

* Massachusetts Institute of Technology, Cambridge, Massachusetts.

† Reynolds Metals Co., Glen Cove, L. I., New York.

sheet. There are development programs of various types along the lines of cladding of shapes; but again, shapes are most intricate.

Going through anybody's extrusion book—and I do not think that is limited to aluminum; I think it applies to magnesium and copper and brass and the other people who are producing brass—it is a pretty complicated proposition.

I am hardly prepared to predict today whether or not clad shapes will be a commercial proposition in the next few years. Certainly they are being thought of, but there are a great many technical problems involved that have to be licked first.

K. R. GUSTAFSON.*—It is my understanding that in your present price book, you are advertising a product known as extruded tubing, and further, that this is a straight-wall product furnished in all types of common and strong aluminum alloys. My question is: What ratio of reduction from billet to tube, and what ratio of reduction from billet to port opening, would you recommend as limitations to produce a 52S or 24S porthole tube?

R. W. ANDREWS, JR.—Again, I have to plead a little ignorance. Being a mechanical engineer, I have seen the aluminum price book perhaps only once or twice in the years that I have been with the Aluminum Company, so you probably know it better than I do.

The extruded tubing to which you refer is substantially straight wall. Your question was a little bit confusing because you referred to porthole. There are several methods of production currently in use.

Now porthole tubing is the bridge type of die tubing referred to by Mr. Winston with regard to magnesium, in which a solid ingot is used. The metal is parted and then reunited at the die.

Generally speaking, extrusion ratios there will run probably from at least 10 to 1, well up toward 50 or more. As far as pressures are concerned, again this is an orifice problem. Along with the orifice problem is the problem of surface friction and flow stress in the metal.

There are all kinds of losses in an extrusion operation. Mr. Pearson's book gives formulas, and Dr. Sachs' book; also, a number of others.

* Revere Copper and Brass Co., Halethorpe, Maryland.

All of them total up the forces required for extrusion. They total them up with a factor attached to each one which has to be determined in each particular case. So there is no mathematical method of prediction of pressures required.

It is obvious that every time the metal has to turn a corner power is required. Consequently, the total force necessary to produce a straight-walled, so-called porthole-die extruded tube is considerably larger than a tapered-wall extruded tube.

I cannot tell you how much, because it will vary almost from application to application. But again, we are not concerned with the force for a particular job. The orifice in the die regulates that.

The steel in the container regulates the maximum force and the maximum pounds per square inch that we can put on the ingot, and if we use a porthole die where the path is devious we are using more of the total power of the press in frictional heat in going around the corners and getting around to the point where the extrusion actually takes place than we do on an ordinary straight extrusion.

There is no mystery about it, but it is extremely difficult to assign values to a thing like that.

MEMBER.—Has 24S been successfully extruded on a porthole die?

R. W. ANDREWS, JR.—Yes, it has; 24S has been extruded successfully on a porthole die. It is not easy, but it has been done and it can be done. It takes a lot of power obviously, but it has been done. 1

J. ALICO.—Perhaps Mr. Andrews could tell us a little bit about the progress that has been made with tapered extrusions and stepped-up extrusions? There has been some literature on it, but I would like to know whether anything more has been done on those processes.

R. W. ANDREWS, JR.—I will take those in the order in which you raised them. As far as I know, tapered extrusions are not offered to the trade. Some of you here who are in the extrusion business (aluminum alloys) may take exception to that statement. There are a few methods of tapering certain sections in an extrusion. In his volume on the extrusion of metals, Claude Pearson shows several methods

in which a mandrel is used which is moved forward or backward and produces a tapered surface. It does not produce a completely tapered extrusion.

Stepped-up extrusions were developed largely for aircraft spars. Large airplanes such as large bombers, judging from the size of the spars, have, I would say, extremely large cantilever bending moments on their overhung wings, which have to be supported by one or more main structural members through the wings, which are called the spars or spar caps. Since the wings are removable, it is necessary to have a rather large attachment, and the attachment in that structural member has been a distinct problem.

Stepped extrusions were developed for that purpose. They consist of two general types; one in which there is a common surface between the extrusion of smaller cross sections and the extrusion of larger cross sections; and one, an uncommon surface type, in which the two shapes are similar but no surface is common to the two.

What happens is this: The proportions of the heavy end to the lighter end are determined by the aircraft designer, because he must take that stepped extrusion and machine it to a continuously tapering piece of metal. Almost always he has to have a bulb on the end of the attachment and the bulb is extremely heavy. That is the primary reason for the use of stepped extrusions. It has saved many thousands of pounds to the aircraft designer.

THE CHAIRMAN.—Now we would like to devote a few minutes to a discussion of the extrusion of copper and brass. I think the time will permit us to come back and ask questions in regard to aluminum and magnesium later, but we want to be sure that the subject of copper and brass has been thoroughly discussed.

E. W. PALMER.*—I should like to ask Mr. Cotter to discuss the causes and possible cures of the extrusion defect of pipe or core?

W. W. COTTER.—The question is: The causes and cures for pipe or core in sections of extrusion?

That comes primarily with solid sections, not so much with tubular sections, unless the wall thickness is very heavy.

The core is caused primarily by the oxidation of surface material in contact with the container walls being drawn into the flow through the die of the center portion of the billet.

It is possible to greatly reduce this flow through scalping of the billet by using a dummy whose diameter is smaller than the inside diameter is smaller than the inside diameter of the container. This may be from 0.050 to 0.100 in., depending upon the alloy, but should not be sufficiently smaller to create any amount of back flow of the metal between the die and the dummy.

The major cause of pipe or core is the inclusion of oxidized surface material from the sides or ends of the billet being drawn into the current of flow of sound metal through the die and failing to weld to this metal.

It is sometimes helpful to resort to multiple-hole extrusion, where several dies are located at points midway between the surface and the center of the billet, so that metal flows into them from both directions.

Another helpful practice is preforming the billet; i.e., upsetting it in the container until its exterior surface is in complete contact with the interior surface of the container, pausing momentarily to permit uniform chilling of this surface and then proceeding to complete the extrusion. By so doing, the smaller dummy will tend to center itself, and leave a complete cylindrical shell in the container, which later is removed.

Even with these precautions, if extrusion continues until the butt end of the unextruded material is too short, pipe or core metal will be drawn into the stream from the ends of the billet and will result in unsound ends of the extruded section, which must later be discarded.

Long rods weighing as much as 500 lb. have been successfully made by single-hole extrusion through dies of large diameter when these practices have been followed.

Tubular formations are not so apt to pipe or core because the material flows both from inside and outside into the annular space between the die and the piercing mandrel.

Upsetting or preforming the billet before piercing is desirable in the extrusion of tubes, in order to minimize eccentricity.

Rods have been made on a tube machine by inserting the piercing mandrel only part of the

* American Brass Co., Waterbury, Conn.

way into the billet and holding it in this position. Material is then extruded around the end of the mandrel through the die and forms a solid rod.

There is some indication that in the extrusion of fairly large rods by this method there may be a reduction in resulting scrap. An engineer from South Norwalk attempted to demonstrate this on one of our older style machines, and he did show that there were some possibilities in that direction. But in general multiple-hole dies, plus scalping, plus preforming makes it possible to reduce pipe tendencies very largely.

C. R. MARSLAND.*—Does the outside defect on extrusion occur only on rather small reductions or is it common to reductions of a large percentage? In the paper there was a reference to inverted extrusion as giving an outside blistering defect. Is that common to all reductions, or does it occur only when a small reduction is taken?

W. W. COTTER.—Inverted extrusion has not been generally practiced in this country. It does lead to a tendency in the oxidized surface material to appear on the surface of the extruded rod as blisters when scalping is not used because of difficulties in separating the tools from the discards.

I do not know a firm today that is using inverted extrusion on any of the common products in the brass and copper industry. I think it has been superseded and I doubt whether it will be utilized again in any of our common materials such as market brass rod, rivet wire, bronze rods and engineering materials so commonly demanded at the present time.

It is diametrically opposite to the first subject I discussed, and I do not think it is a question worth thinking about or carrying forward, because I do not see any future to an inverted extrusion with the present capacities and types of equipment, with which we can do so many things in combination to get the very best results in all commercial forms of material.

W. L. CLARK.—May I say a word about coring. I do not think Mr. Cotter brought out the fact, which we all recognize, that coring or pipe is the result of drawing an oxidized surface

from the billet into the flow of extrusion, and the point he raised in upsetting the billet first means that the billet surface is somewhat chilled by contact with the inside surface of the container, which necessarily is colder than the billet in brass extrusion.

He brought out the point that we use a smaller dummy block, which really broaches out the center portion of the billet and leaves that oxidized surface in contact with the container, so that no surface material is drawn into the extrusion until the remaining billet length is so short that some of the surface from the dummy block and from the face of the die is eventually drawn in.

MEMBER.—I am interested in an extruded bar of a definite size, from any material—magnesium or aluminum. I am interested in the bar stock, not the shape bars or rods which are extruded through approximate size, and through the machine to a definite size. I am interested in a $\frac{1}{2}$ -in. diameter bar to reduce it to a much smaller figure. During that machining, the removal of stress is caused in a large measure to bulb. Are extrusions better or worse than rolled stock from that standpoint?

W. W. COTTER.—I can start the discussion by saying that very different grain structures are obtained in the rolling operation and in extrusion.

Basically speaking, the extrusion process is all compression. The materials are not in tension when you work them, and when you roll them. Consequently, I will say that in extrusion we obtain a very fine short-grained material. The greater the reduction, the finer the initial grain size. If you want to further refine that extruded grain, you must do it by drawing, rolling or otherwise, as is common practice in producing small diameters of wire or small rods.

Extruded products have their limitations, just as rolled products do. We get with this fine short-grained structure the ability of materials to stand extreme spinning, heading or other operation, but we do not get the virtue of a rolled product.

An illustration of that is a motorboat shafting, where torque and fatigue must be considered. With respect to the question of size of the products with the skin removed—those are physical conditions, which might come from the machining operation of the drawing operation,

* Handy and Harman, Bridgeport, Connecticut.

or lack of proper preparation of the base material.

Extruded metal even carries strains, just as rolled material carries strains in its cooled but hot-worked state, and those strains must be relieved if you hope by corrective measures to get a straight bar.

It would be possible to make one product into a finished product interchangeably by using the same finishing methods, but the stock must be prepared before the finishing methods are applied to get the physical properties at the end.

You can heat-treat and normalize and cold-work such products to get any condition of the final product.

A. B. CUDEBEC.*—I imagine a number of people here this afternoon hoped that we would have information conveying the latest development in connection with the extrusion of the nickel alloys.

Mr. Clappier, of the International Nickel Co., who expected to be a member of the Panel Board, could not be here, and I would therefore ask your indulgence for a moment to give you an over-all picture, as I understand it, of the present development of nickel-alloy extrusion.

Nickel alloys have been commercially extruded by only one company, the International Nickel Co. This is a new field and it has been working successfully with a large production for about 18 months. I believe this has been devoted very largely for war purposes.

The problems that enter into nickel extrusion are quite different from those with either of the light metals, or the copper and brasses, in that temperatures are much higher. Nickel alloys do not extrude below 2150° to 2250°.

Unfortunately the temperature band at which nickel alloys will extrude is very narrow—perhaps not wider than 50° or under.

Therefore, temperature controls must be held very close. Moreover, working with temperatures between 2150° and 2250°F., the question of heat in the tools and in the machines is most critical. Therefore, extrusion of nickel alloys, and also of the stainless steels, must be performed quickly. Extrusion of these alloys has been on a commercial scale for a number of years in Europe.

Every possible means must be found to get the ingots or billets (I do not know which) into the extruder and out of the extruder in the shortest possible time, otherwise the tools and dies will become so hot that they will deform. This minimum of time is largely a question of mechanical development.

A considerable amount of time, effort and thought has been put on the speed with which to operate extruders working upon nickel alloys. The process, however, is essentially the same as the extruding of light alloys and brasses. It seems likely that the nickel alloy extrusions will find their way into commerce on a broad scale, and presumably stainless steels will also. The process in Europe, as I say, has been commercialized for a number of years and so far as I know, the difficulties have been removed.

Are there any other questions on extrusion? We would be glad to have one or two more questions.

MEMBER.—During the war we used large quantities of rectangular tubing, which was drawn from extruded round tubing. That tubing gave trouble with a belly action at the ends. Is it possible to extrude directly such rectangular tubing, so that a drawing operation would not be necessary—in copper and aluminum alloys? The long dimension is about double the short dimension.

R. W. ANDREWS, JR.—Over-all dimension, wall thickness?

MEMBER.—Well, say at a range of 1½ by 3, with a 50-mil wall on down in the smaller size.

R. W. ANDREWS, JR.—It can be extruded, but not easily. Obviously, that is an internal strain problem, and, as has been indicated in the answers to some of the other questions, the problems of internal strain have to be attacked pretty much on the merits of the particular case involved.

When there are sharp corners, there are not only internal strain problems but stress raiser problems, and they are not problems that lend themselves to an answer from a platform. I am afraid they have to be taken one at a time on their own merits. I am afraid, however, that merely shifting from drawn tubing to extruded tubing would not solve your problem.

* Hydropress Inc., New York, N. Y.

Symposium on Powder Metallurgy

(Chicago Meeting, February 1946)

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Seminar on the Theory of Sintering

By F. N. RHINES,* MEMBER A.I.M.E.

(Chicago Meeting, February 1946)

I. An Outline of the Theory of the Sintering of Pure Metal Powders

SINTERING may be defined as the process by which powders bond themselves into coherent bodies, usually, although not necessarily, under the influence of pressure and elevated temperature.

For the sake of clarity and simplicity, the present survey will exclude from consideration the sintering of mixed or alloyed powders, with attendant complications, but at the risk of overlooking information of general applicability. Sintering in the presence of a liquid phase is thus automatically eliminated. The sintering of alloys involves much additional subject matter and deserves separate consideration.

Since the literature of the subject is extensive and widely scattered, it will not be feasible to consider the contributions individually. Instead, the subject matter will be classified according to experimental observations and theory, and will be presented in summary form. It should be noted that the appended list of references does *not* constitute a complete bibliography; it includes only those works quoted below. More extensive bibliographies¹ are included in several of the references; see particularly references 7, 9, 28, 34, 38, 50, 52, 54, a "Bibliography on Powder Metallurgy" published by the Library of Congress and a pamphlet published

by the Metals Disintegrating Co. entitled "The Field of Powder Metallurgy and Bibliography."

II. Summary of Experimental Observations

The following classified list is composed of general statements of established fact derived from the experimental results reported in the published literature. A few contested observations are included, because of their potential importance; these are labeled as such. Any satisfactory and complete theory must be capable of explaining all of the uncontested facts. Obviously, some important facts may be missing from this list and these may hold the key to the correct explanation of the sintering process, but the possible lack of such material should not deter attempts to understand the subject on the basis of what is available here.

A. The Initial Bond at Room Temperature

- a. To a limited extent uncompressed powders and massive metals adhere at room temperature.²⁸ Clean tin powder forms a weak "cake" on standing at room temperature, the strength increasing with time. Clean gold surfaces adhere on light contact,²⁸ as do those of many other substances, including nickel.²⁷
- b. Upon compression the strength of the bond is increased progressively.²⁸ There is a limit of pressure

Manuscript received at the office of the Institute April 15, 1946. Issued as T.P. 2043 in METALS TECHNOLOGY, August 1946.

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²⁸ References are at the end of the paper.

above which no substantial increase is observed; indeed, at very high pressures there are complications which appear to be associated with entrapped gases.

- c. **Surfaces of powder particles are uneven on a microscale as well as on a coarse scale**⁵⁰ and, therefore, are presumed to touch opposing surfaces only at points even after considerable compression. This statement is based upon electron microscope studies.
- d. **Low temperature during compressing lowers the strength of the compact; it is equivalent to lower pressure at room temperature.**³¹ Lower density results unless increased pressures are used. Conversely raising the pressing temperature decreases the pressure required to achieve a given density.^{46,17,8}
- e. **Surfaces of powder particles may be covered with oxide films, which interfere with bonding, the more so the thicker and stronger the film.**^{2,28,50} Oxides can themselves be bonded by compression, but the resultant briquette is weaker than that of a clean metal, although more nearly similar in strength to a compact made from oxidized powder.^{44,25} Gold, which forms no oxide, bonds most easily, while lead is difficult.²
- f. **Adsorbed gases on the surface of the powder interfere with bonding.**²⁸ Hydrogen may adsorb on copper to a calculated depth of as much as 100\AA .⁵⁰ Large volumes of gas can usually be removed from powders by evacuating.³⁹ The tendency of clean nickel surfaces to adhere in vacuum is greatly diminished by the admission of hydrogen.²⁷ Gold, which ordinarily carries no oxide, bonds more readily in vacuum and the same is true of other metal powders. The increase in the ease of pressing in vacuum is particularly noticeable with fine particles that present a maximum of surface. In vacuum pressing laminations diminish.²⁴
- g. **Water mixed with the powder may increase the density reached with a given compacting pressure.**³⁸ After drying, the compact has higher strength than when pressed dry at the same pressure (first used by Wollaston). Some so-called "bonding agents," such as paraffin, produce a similar effect.⁵⁴ Powder "lubricants," such as stearic acid, behave similarly.²⁸ (These are all presumed to be lubricating effects.)
- h. **Powers of hard metals produce a weaker and less dense compact at a given pressure than do powders of softer metals.**²⁸ Cold-worked powders require higher compacting pressure for an equivalent strength and density than do annealed powders.²⁸
- i. **Fine powder requires a higher compacting pressure to produce a given strength and density**²⁸ (a contested observation). Fundamentally, fine particles of uniform size should be expected to pack to the same density as uniformly coarse powder; the effect therefore is to be associated with other than purely geometrical factors—perhaps to adsorbed gases and oxide films.²⁸ Mixed powder sizes give higher density than any uniform particle size.²⁸ The size of the voids remaining after pressing, of course, decreases with the particle size.²⁸
- j. **Particle shape influences the strength and density of the compact; irregular shapes yield the highest density, flakes the lowest (contested observation).**²⁸ This con-

cept is difficult to evaluate because of the complications arising out of the range of shapes used, variations in shape within a given powder, changes in shape during pressing, and the simultaneous occurrence of other variables, such as differing degrees of cold-work as between irregular and flake powder.

k. **Strength and hardness of the compact increase with the density, but the hardness increases more rapidly.**^{29,59} Hardness may exceed that in cold-worked metal (Cu), while strength rarely approaches that of massive metal;²⁸ electrical conductivity also increases with rising density.²⁸

l. **Localized melting is not involved in the bonding of powders at room temperature.**⁴⁵ Early investigators were inclined to ascribe the cold-welding of powders to the heat of friction at points during pressing.^{13,23} This has been shown to be unnecessary.²⁸

B. Sintering—Effects of Temperature

a. In general, the density increases with an increase in the sintering temperature, but this statement is subject to reservations as shown in succeeding paragraphs.^{28,21} The refractory metals tungsten and molybdenum exhibit the most regular behavior. Unpressed or lightly pressed powders tend to behave most regularly. Vacuum pressing and vacuum sintering also tend to make behavior regular. In general, also subject to reservations, the strength of the compact increases with pressure. Anisotropic property effects and differences in density from point to point in the compact tend to diminish with rising sintering temperature.^{4,38}

b. **There is a temperature, usually associated with the "recrystalliza-**

tion temperature," at which sintering first becomes very rapid and at which the major structural and property changes are observed, when a compact is gradually heated through the range from room temperature to just below the melting point.^{34,28} Some have said that sintering does not occur below the "recrystallization temperature," but this is clearly a case of an insufficiently sensitive test for sintering.⁶² Oxides behave in the same manner, but their temperature of rapid sintering (and "recrystallization temperature") is significantly above that for the corresponding metals.^{25,44} Oxidized metal powders require a higher sintering temperature than clean powders. The "recrystallization temperature" referred to here is really that of observable grain growth in the powder compact and is considerably above the recrystallization temperature found in cold-worked massive metals.

c. **First indications of an increase in the adhesion between loose powder particles, and in the strength of compacts, are felt below 200°C. for all metals except those of extremely refractory nature (W, Mo, Ta);**^{58,59,21,14} and at the same time there is a decrease in density (increase in porosity) of compacts in heating to 200°C.^{4,22} It is indeed noteworthy that Tammann⁵⁸ found that loose powders of Ag, Cu, Fe, Al and Zn all begin to adhere (in a stirring test) within the same narrow temperature range 140° to 148°C. This is a strong indication that something not closely associated with the properties of the individual metal is causing the effect (the removal of adsorbed gases is suggested).⁵⁸ Other proper-

ties, such as hardness and electrical conductivity have also been found to exhibit a substantial increase up to 200°C.^{59,21} Cold-working (milling) the powder does not alter these effects.⁴ Some instances of a rise in density to 200°C. have been reported, but these are to be associated with pressing at temperature.²¹

- d. A second, very marked, decrease in density frequently occurs at or above the "recrystallization temperature," particularly in compacts made under very high pressure.^{6,59,98} This may be accompanied by a drop in the strength of the compact. Where powders of the same screen analysis are compared the expansion is the greater the higher the compression ratio of the powder.¹¹ Where various size ranges are compared the effect is the more pronounced the coarser the powder.⁴ Extreme cases in which expansion occurred throughout the temperature range of sintering have been reported.^{4,5} (With one notable exception,⁵ all writers on the subject agree that high-temperature expansion is to be associated with the evolution of dissolved or combined gases either with or without the cooperation of reducing furnace gases).
- e. Normal volume changes associated with thermal expansion and crystallographic transformations occur in loose powder masses and compacts, somewhat modified by the density changes associated with sintering in the course of temperature change.^{32,36} Only the volume changes associated with crystallographic transformations are known to alter the density permanently—iron, at 900°C., exhibits a large decrease in density, which remains after cooling.^{49,28}

- f. Individual angular powder particles tend to spheroidize at temperatures often several hundred degrees below their melting points.^{2,50} Even large pieces of metal have been observed to lose sharpness at corners when held at high temperatures below the melting point.

C. Sintering—Effects of Pressure

- a. Pressure beyond that exerted by gravity is not essential to sintering;^{50,49,10,51} see above, section Aa. The finer the powder, the more rapidly does sintering (shrinkage) take place.¹⁰ In general, the sintering of loose powders is slower than that of compacts.
- b. Under constant sintering conditions density increases with rising compacting pressure^{38,21} up to a certain limit, above which density and associated physical properties may decrease.^{5,26,47,33,49,28,20} When different types of powder of the same metal are compared, compacts of equal density suffer equal shrinkage during sintering regardless of the pressure used;⁵ (this points to density rather than pressure as being the critical factor). When compacted at equal pressure, the lower the density of the compact, the greater the shrinkage;⁵ this effect is observed in all of the softer metals, including Cu, Fe, Au.^{28,49,33} The decrease in density with high compacting pressures is associated by most investigators with the trapping of gases (see section Bd).
- c. Hot-pressing produces a compact of higher density than is obtained when like pressure and temperature are applied separately.^{3,46,17,18} Densities approaching the theoretical limit are obtained only by the use of relatively high pressures at

temperatures well within the normal hot-working range.^{18,17} Hot-pressing followed by sintering is not observed to result in growth of the compact at temperatures where growth would otherwise be expected.¹⁷ Below the normal recrystallization temperature the effects of hot-pressing may be very slight.²⁶

d. Repressing after sintering increases the density of the compact and a subsequent resintering operation may cause the density to approach the theoretical maximum.¹⁹ Copper so treated attains the physical properties of normal hot-worked copper.^{16,60}

e. Work-hardened powder sinters at a slightly accelerated rate and the effect of pressing in work-hardening the powder can sometimes be detected by this criterion.^{10,5} In general, the work-hardening of powder by milling is more effective than work-hardening by pressing.⁵ Because of the smallness of the effect its existence is doubted by some.⁴ Perhaps the most noticeable effects are found in the sintering of loose powders¹⁰ and in the lowering of the temperature of recrystallization.^{9,55}

D. Sintering—Effects of Time

a. The rate of sintering is most rapid at the beginning and proceeds at a decreasing rate (constant temperature).^{11,33,25,6} In general, the experimental data show density still increasing at the end of the test. The importance of time is most evident at low temperatures of sintering. The progress of sintering with time is not always regular—an initial period of expansion followed by shrinkage, and then expansion again, can sometimes be observed.¹¹

b. Long sintering times may result in more lowering of strength associated with grain growth than increase of strength associated with shrinkage⁴⁹(see Section *Ga*).

E. Sintering—Effects of Gases and Other Foreign Substances

a. Sintering atmospheres capable of reducing the surface oxide films on the powder and of preventing further oxidation generally assist sintering; i.e. increase the strength and density of the compact.^{50,28} On the whole the interference of oxide films with sintering is not as serious as might be supposed. While the maximum effects of sintering are not attained in the presence of oxide films, considerable density increase may occur in air sintering, particularly in hot-pressing.²⁸ Some noble metals give better results in air sintering.²⁶ Oxides contained within the powder particles are not easily reduced during sintering and are thought to contribute to growth during the late stages of sintering.³

b. Adsorbed and absorbed gases interfere with sintering by causing growth of the compact when they are evolved.^{28,59,62,3,26,22,38} When powders are heated in vacuum substantial quantities of gases are always released,^{39,57,28} running as high as 1000 times the volume of the metal (at standard pressure).²⁸ The rate of gas evolution tends to increase with temperature and becomes very high at the recrystallization temperature.⁵⁷ The gases found are of all kinds found in the atmosphere,^{28,39} but it is believed that oxygen, in combined form, constitutes the largest single source of gas.³⁹ Vacuum sintering sometimes yields higher density with copper

than is obtained by the use of hydrogen;^{49,16,15} in other words, hydrogen may tend to delay sintering. Vacuum-sintered copper sometimes develops some large pores presumably as a result of the release of trapped gas late in the sintering process.¹⁵ Virtually all growth phenomena observed during sintering have been attributed by some to the release of gases.^{62,3,26,22,59}

- c. Gases may affect powder metal compacts in other ways, as by changing the rate of grain growth in tungsten.⁵⁵
- d. Solid foreign matter (in addition to oxides) may impede sintering.²

F. Effects of Sintering upon Structure

- a. Grain growth across the original interparticle boundary is usually observed after sintering at a high temperature.^{49,60,50} This occurs even with uncompacted powders and even in the absence of cold-work, and, thus, is not necessarily the result of recrystallization.⁴⁹
- b. The temperature of rapid grain growth is apparently independent of the pressing conditions, or of the preliminary cold-working of the powder; it lies at approximately two thirds of the melting temperature of the metal (three fourths of the absolute melting point.)^{40,42,28,38,49} Much confusion has arisen through the misunderstanding of the difference in the temperature at which normal recrystallization can be detected and that at which substantial grain growth is observed. Grain growth may be impeded by many factors including impurities and porosity.¹⁵
- c. The temperature of normal recrystallization is the lower the more the powder is cold-worked prior to pressing, or the higher the compacting pressure used.^{48,38,49,9,55} Annealed powders, loose or pressed, generally exhibit a higher recrystallization temperature, as detected by X-ray diffraction, than do milled powders. Since recrystallization is usually seen first at the interparticle boundary, it is supposed that this is proof of localized cold-work in this region⁵² and is responsible for the usual moving of the recrystallized grain boundary away from the interparticle boundary. These effects are observed in all classes of metals.
- d. The coarser the powder the finer the ultimate grain size.^{36,55,56,49,5} This behavior has been reported in both tungsten and iron. It is attributed to the lower temperature at which recrystallization occurs with fine powders,⁴⁹ which presumably suffer more severe distortion in pressing. It is thought by some that grain growth is also faster in fine powders.⁵⁵
- e. Pores tend to change from an angular to a spherical form with long sintering or high temperature.^{28,6} This change is apparent in micrographs scattered through the literature, and is also shown by experiments that measured the time decrease in the continuity of porosity.²² Powders, such as tantalum, that tend to continue to release gas after long sintering may produce "puffed bars," showing that the continuity of porosity has disappeared.²
- f. Pores tend to diminish in size and disappear with long sintering times at high temperature; small pores seem to shrink faster than large pores. This effect can be seen by scanning micrographs scattered throughout the literature, but has not been specifically commented

upon, probably because the very long sintering times required are unusual.

- g.* Oxides trapped in compacts, if not reduced, tend to become spheroidized during sintering.⁶²

G. Effects of Sintering upon Physical Properties

- a.* Strength as measured in a tensile, compressive or bend test tends to increase as the density increases up to the temperature at which rapid grain growth sets in; thereafter, it may decrease or increase, depending upon the relative extent and influence of the opposing factors of shrinkage and grain growth.^{45,49,12,38,12,43} In iron the first drop in strength is observed below the alpha-gamma transformation and is attributed to grain growth. All of the lower melting metals exhibit this effect.
- b.* Hardness tends to reach its maximum value very early in the sintering process and to fall rapidly with the onset of recrystallization.²⁸ Hardness is the only mechanical property that appears to reach values exceeding those in other common forms of the same metal,²⁸ although the special case of tungsten in which the wrought compact is stronger than the cast metal has been cited as an exception.³ Hardness and tensile strength do not regularly follow a parallel course, as in most other forms of metals.²⁸
- c.* Elongation tends to increase more slowly with sintering than other mechanical properties and continues to show increase with time at the sintering temperature after the perceptible changes in other properties have almost ceased.³⁶ This effect has been attributed to the greater sensitivity of elongation

to the shape and size of the porosity (notch effects).

- d.* Electrical conductivity change appears to parallel the density change.²⁸

III. A Composite Theory of Sintering

Since a number of theories of sintering have been offered, but no single theory accounts for the entire range of observations listed in the foregoing pages, it seems best to construct a composite theory including the factors with which substantially all agree, and choosing rather arbitrarily among the connecting links that are in dispute. In this way a complete chain of reasoning will be provided at the start and the conflicting ideas may be discussed with respect to this synthetic theory.

In the following section the principal statements of the composite theory are in bold face type. After each statement of the theory the substantiating evidence from the experimental observations tabulated in the foregoing section are cited. Finally, supporting and conflicting statements of theory, as they appear in the literature, are quoted.

A. The initial bond that appears spontaneously at points of metal-to-metal contact at room temperature is identical in kind with the forces that hold the atoms of a metal crystal in place and give solid metals their strength. This bond differs from that in the sintered material only in the relatively small area of the interparticle surface so joined, and possibly also in distortion of the crystal lattice in its vicinity (a condition that is eliminated by recrystallization and grain growth during sintering).

Cold-welding occurs with little or no pressure when clean surfaces are brought in contact (see II *Aa*). The domain of the bond must be small because powder surfaces are rough on a microscale and may touch only at isolated points (see II *Ad*).

Interfering films of oxides, adsorbed gases and other foreign matter prevent metal-to-metal contact and reduce the occurrence of bonds (see II *Ae* and II *Af*). It is not necessary that melting occur to effect bonding (II *Al*).

Virtually all modern thought on the subject is in agreement with this view. Detailed discussions of the mechanism are presented by: Sauerwald,⁴⁹ Jones,⁵⁰ and Wulff.⁶² Early investigators proposed melting at the points of bonding, caused by localized high pressure, or by friction when powders are disturbed or pressed: Endell¹³ and Hardy.²³ Smith⁶³ proposed that bonding occurs only coincident with a phase change or recrystallization. All of the latter ideas have been discredited by the experimental observations cited above (see Jones²⁸ and Sauerwald.⁴⁶)

B. Pressure serves to redistribute and deform the powder particles in such manner as to increase the conformity of opposing surfaces and, thus, both to increase the number of points of metal-to-metal contact and to enlarge slightly the individual domains of contact bonding. Pressure, and the interparticle movements resulting therefrom, may also serve to dislodge or rupture interfering films of oxides, adsorbed gases and other foreign matter and, in this way also, to increase the number of points of metal-to-metal contact.

The strength of the compact increases with pressure, as might be expected if the number and size of the sites of cold-welding were increased (see II *Ab*). Low temperatures diminish the effects of pressure, high temperatures increase them, corresponding to the expected plastic response of metals at low and high temperatures, with resultant decrease or increase in the number and area of points of contact produced (II *Ad*). Water and other lubricants assist in the production of denser compacts, which are more or less proportionally stronger, as would be expected if by re-

arrangement the powder particles were to develop greater intersurface conformity (II *Ag*). Hard particles produce weaker compacts because of the smaller degree of plastic deformation produced in pressing (II *Ah*). Particle size and shape influence the degree of bonding attained though their effects on total surface area (fine powders with large surface carry more gas and oxide), the relative ease of particle deformation and the ease with which opposing surfaces conform (ref. II *Ai* and II *Aj*).

Again, modern investigators are in general agreement with this view. These matters are discussed by Sauerwald,^{49,50} Jones,²⁸ and Comstock.⁸ There is agreement also that the geometrical interlocking of particles of complicated shape may add somewhat to the strength of the compact.^{49,23} Balshin⁵ says that fine particles do not compact as well as coarse particles because initial welds must be broken to move particles to closer packed positions, but it is difficult to understand how such an effect could differ with size. The concept of welding being facilitated by melting at points of high pressure or where friction occurs^{1,23} is disproved by the slight increase in bonding obtained as the speed of pressing is reduced.

C. At elevated temperatures the initial "point-bonds" grow laterally and the total of void space is decreased by the movement of metal most rapidly into the narrow spaces adjacent to bonds and more gradually into larger voids. The movement of metal is presumed to be accomplished through the action of plastic flow, or of surface diffusion, or of both acting cooperatively under the influence of the energy of surface tension as the major driving force. Where the curvature of surface is greatest, surface tension reaches its highest value and the reduction of the curvature, by filling in sharp angles in the surface, will effect a significant reduction in the energy of the body. Thus, surface

diffusion should be expected to result in a net transfer of metal into the sharp angles adjacent to bonds and the tendency for plastic motion to bring opposing surfaces together should likewise be greatest in these regions. Either of these actions should increase at an accelerating pace with rising temperature, with the result that there will be a relatively narrow temperature range within which sintering will first become obvious to the casual observer. Either action should proceed at a rate diminishing with time. Either action will also be the more rapid the smaller the void spaces and will be impeded by the interference of foreign matter or high gas pressure in the pores.

The common observation of the decrease of density with rising sintering temperature (II *Ba*) is consistent with the increased rate of shrinkage and growth of the bond predicted by the theory. A rapid rate of sintering coincident with observable grain growth and other signs of atomic mobility (II *Bb*) is consistent with the view that sintering proceeds through the action of plastic flow and diffusion. Observations of the spheroidization of individual powder particles at high temperatures (II *Bf*) supports the view that the mechanisms energized by surface tension are capable of producing observable effects. No pressure beyond that required to produce initial metal-to-metal contacts is required by the theory and experiment shows that loose powders will sinter (II *Ca*). The accelerating effect of pressure upon the sintering process (II *Cb*) is predicted by the statement that a reduced pore size should facilitate the movement of metal. Similarly, the accelerating effects of hot-pressing (II *Cc*) and repressing and re-sintering (II *Cd*) are consistent with the present proposal. Although somewhat surprising, the statement that cold-work, as such, accelerates sintering (II *Ce*) is in accord with the theory, for diffusion rates are increased by cold-work. The rate

of sintering should be expected to decrease with time, as observed (II *Da*) because of the decrease of surface-tension forces as angles in pores are reduced. Any foreign substance should, of course, impede plastic flow or diffusion (II *Ea*) and II *Eb*), solids or films by mechanical obstruction and gases under pressure by their opposition to the surface tension forces. The spheroidization of pores (II *Fe*) is a necessary outcome of the proposed mechanism.

While the observations cited above are in conformity with the theory, none serves to prove the action of either plastic flow or surface diffusion or to indicate which process, if either, is dominant. Recent thought, however, is predominantly along the lines described above; see Balke,² Wulff,⁶² Comstock,⁸ Garre,¹⁴ Ritzau,³⁷ and Schumacher and Souden.⁶²

More than 20 years ago, the formulation of the theory was begun by Sauerwald,⁴⁰⁻⁵⁰ who held the view that the major driving force of sintering resided in the potential bonding forces. As the temperature is increased, he said, the atomic orbits are enlarged and some points not initially bonded are bridged by the greater reach of the atomic forces; once formed, these high-temperature bonds persist, and upon cooling produce plastic deformation as the metal contracts. This picture contains the concept of plastic deformation and also an idea not far removed from that of surface-tension forces. He also points out that corrugated surfaces tend to become smooth at high temperature and this action should tend to increase the area and number of contact bonds.

Jones²⁸ view of sintering differs from that of Sauerwald in his contention that the atomic bonding forces become weaker at high temperature, as shown by the lower strength of metals at high temperature, and, therefore, increased atomic mobility alone cannot increase the bonding of powder particles. He sees the forces favoring bonding diminishing with tem-

perature, but the forces opposing bonding (adsorbed gases, resistance to plastic flow as energized by surface tension and perhaps stresses between bonds) diminishing more rapidly, resulting in a net increase in sintering. Again there can be no quarrel with these views except that they are incomplete.

Balshin⁵ alone, among current investigators, holds views in marked conflict with the proposed theory. He views the sintering process as one of balance between forces tending to bring the particles together and those tending to thrust them apart. Only the interatomic attractive forces are thought to act to produce shrinkage (he accepts Sauerwald's mechanism in this respect), while forces tending toward expansion are: the changes in particle shape accompanying recovery, recrystallization, and grain growth, elastic recovery and the evolution of gases (which he relegates to a minor role). No experimental evidence is offered that can be accepted as proof of this theory and it should be noticed that it in no way predicts a spheroidization of porosity.

D. Since the proposed mechanism of sintering is, by itself, capable of predicting no volume changes except shrinkage, growth must be explained by some other process. The major cause of growth lies in the expansion of the void spaces in the compact through the action of gas pressure. At relatively low sintering temperature, gases initially adsorbed on the surfaces of powder particles are partially evolved and the pressure of gases trapped in the compact during pressing is increased through temperature rise until the interparticle openings are expanded sufficiently to permit the escape of the gases. At higher temperatures, remaining adsorbed gases, gaseous products of the reaction of reducing agents with oxides, and dissolved gases, rejected by reason of reduced solubility, produce a similar effect. When the internal gas evolution

occurs so late in the sintering process that interpore channels have been sealed, growth is exaggerated, particularly when the temperature is sufficiently high to permit extensive plastic flow. This effect probably is produced chiefly by gases that do not diffuse rapidly through the metal. Occasional or lesser causes of growth may reside in stresses established by the irregular occurrence of crystallographic transformations, stresses established by irregular temperature change or the irregular relief of internal stresses.

It is well established that powders exposed to the atmosphere always carry on their surfaces very considerable quantities of adsorbed gases (II *Af*) and usually combined gas, as well, in the form of oxide films (II *Ae*). It is recognized, too, that adsorbed gases are released as the temperature is increased (II *Bc*) and that adsorbed gases interfere with sintering (II *Eb*). Combined gases may be released by reaction with reducing agents at elevated temperatures (II *Ea*). Growth is most pronounced under circumstances that, in the absence of gases, should be expected to favor the most rapid sintering (sealing of interpore channels), such as: with the use of very high compacting pressures (II *Cb*), with sintering at the highest temperatures (II *Bd*) and occasionally after very long sintering times. It is known that the voids in the compact tend to become spheroidized with sintering with an accompanying disappearance of connecting channels (II *Fe*). Oxides contained within the powder may remain partially unreduced through the sintering process, providing a potential source of reaction gases until late in the process.

With the exception of Balshin⁵ all of the writers whose works were consulted affirm this view of the growth process. The dominant role of gases may be regarded as well established. Balshin does not deny the effect of gases, but relegates it to a minor place, attaching greater importance

to the presumed effects of crystal growth and allied mechanisms.

E. Recovery, recrystallization and grain growth may be regarded as proceeding in a normal manner if due allowance is made for the influence of special geometrical factors peculiar to powders and powder-metal compacts. In the pressed form the powder particles will be more severely cold-worked on their surfaces at points of interparticle contact than they are on their inside, because of the flattening of surface corrugations. As a result, recovery and recrystallization may be expected to begin chiefly at the points of particle contact, resulting in the common formation of recrystallized grains growing across the original particle interfaces, and resulting also in a somewhat uneven relief of internal stresses. It follows, also, that these processes should be sensitive to the powder particle size, which affects both the amount of interparticle surface and the breadth of the range of cold-working from surface to interior of the particle. Somewhat related effects should be associated with the particle shape and the mechanical properties of the metal of which the powder is composed. Grain growth will be limited essentially to the powder particle size until sintering has progressed so far as to provide substantial bridging between particles, whereupon larger grains may grow. As a result of this condition, the temperature of rapid grain growth will appear to be coincident with the temperature of rapid sintering. Since rapid grain growth is thus impeded by a network of voids, it follows that it should not be responsive to the effects of cold-work that are destroyed at temperatures well below that of rapid sintering and, therefore, should be sensitive to the pressure of compacting only to the extent that sintering is accelerated by denser compacting. Unreduced oxides and other foreign bodies may be expected

to spheroidize during sintering in the normal manner.

In fully sintered compacts, or loose powder masses, the grains grow across the original particle boundaries and are often much larger than the original particle size (II *Fa*). The temperature of rapid grain growth is *insensitive* to pressing conditions and usually coincides with that of rapid sintering (II *Fb*), which generally is above the temperature of rapid grain growth in massive metals. The temperature of normal recrystallization is *sensitive* to pressing conditions (II *Fc*). Particle size influences the ultimate grain size (II *Fd*). (Smithells⁵⁴ attributes the growth of large grains in tungsten made from fine powder and of small grains in tungsten made from coarse powder to the rate of grain growth rather than to the rate of nucleation; i.e., interfering voids are removed earlier where the particle size is fine.) Oxides spheroidize, if not reduced, during sintering (II *Fg*).

The theory of grain growth during sintering has been discussed extensively only by Sauerwald,⁴¹ whose views are incorporated in the statements above. The effects of impurities on grain growth (II *Ee* and others not quoted) appear very complex; they have been discussed to a limited degree by Smithells.⁵⁴

F. Late in the sintering process the major structural changes are caused by body diffusion of metal from the exterior surface of the compact, or powder mass, into the spheroidized pores, thus reducing their diameters. The driving force is again derived from the difference between the low surface energy (surface tension) of the exterior surface (small curvature) and the high surface energy of the pores (sharper curvature) causing a net diffusion toward the pore. Small pores, having the highest surface energy will be filled more rapidly than larger pores. Those pores near the surface of the piece should be filled before those near the center.

Porosity diminishes with time at the sintering temperature and the small pores disappear long before there is observable shrinkage of the large pores (II *Ff*). "Puffed bars" appear to result from the entrapment of gases within voids after all openings to the surface have been sealed, suggesting that pores close more rapidly near the surface. After repressing when the pores have been flattened, they disappear almost quantitatively in short time (II *Cc* and *Cd*).

This subject has received little attention in the literature and no theory has been proposed.

G. The changes in physical properties accompanying sintering are to be associated with the structural changes described above and do not, in themselves, constitute a part of the theory of sintering. The correlations between structure and properties have been described in section (II *G*) above.

RESEARCH NEEDS

Although virtually all the experimental observations cited appear to support the theory just outlined, a critical examination of the logic employed will reveal that few of the major tenets of the theory have the support of direct evidence.

Thus the concept of points of bonding is arrived at indirectly and the associated idea of the multiplication and enlargement of the bonds during pressing is supported by no direct observation. No one has yet examined an individual bond. Similarly, there is as yet no real proof of either plastic flow or diffusion during sintering; here, again, the evidence is merely supporting, but not directly so. Only the effect of gases in causing growth during sintering appears to be on really firm ground and, even here, many details are lacking.

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DISCUSSION

(Lee S. Busch presiding)

F. N. RHINES.—I want to take just a moment to get the discussion started by saying a little bit about what this review seems to me to say concerning research needs. Very little in the theory as set down is really proved by any of the experimental information upon which it is based. The proof is chiefly indirect. We do not, for example, have an absolute proof of the nature of a bond. We need to devise a scheme for looking at bonds before we can really feel that we know what they are.

Also, as I pointed out a little earlier, the ideas concerning the possible effects of plastic deformation and diffusion in closing the channels between the pores are really shots in the dark. They look pretty good and they seem to fit the evidence that we have, but we do not have any clear-cut proof that diffusion is going on, and in a way that would account for these effects; nor do we have any clear-cut proof, as yet, that plastic deformation is taking place during sintering. Actually, the answer might be 100 per cent one way or 100 per cent the other way, or a sharing of the two effects, or neither. Therefore, we need some critical experiments to help us distinguish these mechanisms; perhaps first to show whether the mechanisms actually operate and, if they do, to tell to what extent each may be involved.

In order to give you an idea what kind of thing I should like to see come out of our subsequent discussion, I should just like to make two or three research suggestions. One is this: In order to get anywhere quantitatively with the proposal with regard to diffusion, we should know something about the rates of surface self-diffusion. These could be measured very easily. Today a variety of radioactive isotopes are available, and I think that it would make a very neat research project to measure surface self-diffusion rates with these.

A second thing, which I have been working on a little bit myself, is a metallographic study of the rate of shrinkage of pores during long sintering. What I propose to do is to make a

record of the total number of pores as a function of sintering time, and of the size distribution measured in terms of cross-sectional area or perimeter, and in that way get information that will help to show what sort of mechanism, exactly, we must describe to account for the shrinkage of porosity with time. We need to know more in detail about just what it is that we are describing when we set up a theory of sintering and I hope that this project will assist in this respect.

A third suggestion is the metallographic study of the influence of the kind of entrapped gas upon the rate of pore shrinkage. This may be a matter of secondary importance, but it would be interesting nevertheless to know whether a compact containing entrapped hydrogen compared with another compact containing nitrogen would exhibit shrinkage at different rates.

J. E. DRAPEAU, JR.*—You are to be complimented, Dr. Rhines, for your splendid review of the present status of the theory of sintering of metal powders. Let us look at changes similar to sintering, such as crystal growth.

For example, large crystals may be grown from a saturated solution of copper sulphate containing an excess of small crystals and a single large crystal. We have an equilibrium condition. It has been explained that the rate of solution of the small crystals is greater than the large crystal.

What happens after a few days? The small crystals dissolve and the large crystal grows larger. The end result is that the small crystals have been transferred to the large crystals. Thermodynamics calls this single-crystal saturated solution a more stable saturated solution. Large crystals, or large grains, may be a more stable sintered state than small grains, all other things being equal.

Another example of crystal growth is present in electroplating or electrolytic deposition of metals. The size of the crystals may be retarded through so-called organic addition agents to the electrolyte; for example, glue.

In electrodeposition good bonding of metal crystals is obtained at room temperature without melting. Is it not similar to sintering of metal-powder particles without melting?

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In production of lead storage batteries, addition agents, known as expanders, are added to the negative plates to improve cold capacity. The expanders retard the tendency to develop large lead sulphate crystals during discharge and small lead particles during charging stage. Here again is a phenomenon that in many respects has many features like the bonding, sintering, or recrystallization of metal powders below the melting point.

We are all familiar with crystal growth in tungsten-wire filaments and how it was retarded with thorium oxide. Seriously, thermodynamics can give quantitative, precise information concerning stability of substances, reactions, and other subjects.

Thermodynamics will not tell us the relative rate of physical or chemical changes in substances. Furthermore, it does not explain the stages or detailed nature of the change or process. Thermodynamics gives information on the stability (free energy) of a substance when data on specific heats, heat formation, heats of crystallization, entropy, and other essentials are available.

What I wish to bring up is the use of thermodynamic reasoning in approaching the theoretical aspects of sintering. Thermodynamics in powder metallurgy suggests surface free energy (stability) of different faces of crystals and related phenomena in the study of grain growth. Which of the following is the most stable system:

Small particles or large particles?

Annealed particles or cold-worked powders?

Irregular surface particles or smooth-surface particles?

Soluble impurities in metal particles or pure metal particles?

Foreign film coatings on different crystal faces of metal particles or free clean crystal faces (surfaces)?

Particles of metal?

Loose compacted particles or densely compacted particles?

Thermodynamics tell us that:

1. Systems at different pressures or densities will tend to come to equal pressure or density.

2. Systems at different temperatures will tend to come to equal temperature.

3. Systems at different concentrations tend to dilute themselves to a uniform concentration.

4. Systems under different strains (energy levels) tend to equalize themselves.

Thermodynamics may not tell us the mechanism of how the (changes) sintering occurs, but it may aid us in predicting what will tend to occur.

I should like to ask Mr. Wulff if he has noted any effects of the rate of compressing metal powders on the density of the green compacts. (Rate of compressing might be considered as rate of cold-working of the powdered-metal compact prior to sintering.)

F. V. LENEL.*—I should like to add a few remarks to what Mr. Drapeau brought out; namely, the determination of forces by thermodynamic calculations. I wonder, however, whether calculations of the difference in solubility between large and small crystals would help us in one component system that is under consideration here. Such calculations play an important part in Price, Smithells, and Williams' theory of the sintering of the so-called "heavy metal," a tungsten-copper-nickel alloy,† but here we have the case of a heterogeneous system containing a liquid and a solid phase rather than a one-component system.

On the other hand, are there not quantitative data available on the forces that seemingly are involved in sintering one-component systems? In other words, do data exist on the forces of surface tension on the one hand and the forces that resist plastic deformation (yield strength) on the other, over a range of temperatures? Such data should make it possible to substantiate the theory of sintering as given by Dr. Rhines. I do not know the literature on these matters well enough, and I am, therefore, directing this question to Dr. Wulff and Dr. Rhines.

JOHN WULFF.‡—Permit me to congratulate Dr. Rhines for his very able presentation of the theoretical data on sintering. Of the three theories discussed, certainly the one that attributes the major shrinkage that occurs during sintering to diffusion deserves closer

* Moraine Products Division, General Motors Corporation, Dayton, Ohio.

† G. H. S. Price, C. J. Smithells and S. V. Williams: *Jnl. Inst. Metals* (1938) 42, 239 ff.

‡ Massachusetts Institute of Technology, Cambridge, Massachusetts.

perusal. If shrinkage is wholly dependent on diffusion, there should be a net transfer of material from the outer layers of the compact to the interior during sintering. In other words, metal moves in and the pores move out. At present, there is no definite experimental information that justifies this picture of sintering, and Dr. Rhines is certainly right in suggesting that some diffusion experiments are needed to clear up this point.

Some years ago I felt more strongly for diffusion than I do now. If there is a net transfer of material from the outside of a compact to the inside during sintering, why should a diamond-inscribed mark on the surface of a compact still exist after excessive shrinkage has taken place during sintering? Likewise, the observation that shrinkage begins at the outside of the compact rather than the inside is discernible on pressed compacts rather than in briquettes that have been sintered without prepressing. In this morning's discussion, Dr. Seelig and I suggested* that excessive shrinkage of the exterior of a compact may be due to: (1) the greater densification of the surface skin of pressed specimens, and (2) the more rapid heating of the outside of the compact during sintering.

F. N. RHINES.—I do not care what I see when I look at the sample after it is sintered one hour. All I am interested in is the difference between what I see after one hour and after 100 hours. Maybe this will eliminate those effects.

JOHN WULFF.—To be sure, observations after long sintering times are more important! For long sintering times at high temperature such inhomogeneities due to pressing should be eliminated. At the same time such disturbing variables as adsorption and oxide skins should be eliminated if long-time sintering data only are used.

L. S. BUSCH.†—Would anyone else like to discuss this? Certainly someone must want to argue with our colleagues. Dr. Wulff has published an excellent little book, *The Physics of Metals*, in which he goes into the thermo-

dynamics of the regular metals mostly. I consult that little book frequently, and almost invariably it helps me, because he treats only of fundamentals, and after all, that is what we are trying to get at here. We are trying to lay the thing wide open and find out why it works and what we can do to make it work better.

F. N. RHINES.—Let's have some ideas on how to prove that plastic deformation takes place during sintering, if it does. Is there any way we can put a grid in compacts?

JOHN WULFF.—We are using grids of lead to study plastic deformation during pressing. Work has been started in using grids of gold and silver wire in studying the shrinkage that occurs during the sintering of iron compacts. It is hoped that this procedure will shed some light on whether the shrinkage occurring during sintering is more of the nature of a plastic deformation.

In order to bring others into the discussion, permit me to ask Mr. Langhammer whether he has any ideas concerning the simultaneous longitudinal growth and axial shrinkage during sintering of cylindrical specimens.

A. J. LANGHAMMER.*—You have caught me rather unprepared, as my technical colleagues are not with me. My comment on the subject is this: It is implied, if not stated, that powders shrink upon sintering. That has not been our experience, and that is quite true relatively of iron powder also. In general, iron powder compacts upon sintering and shrinks, but it shrinks at different degrees, depending upon a group of factors other than sintering, or sintering conditions. We have experienced wide variations of growth or shrinkage, and it is a fallacy to conclude that in the sintering of iron there is a definite shrinkage—that is, iron powder alone. I am not speaking of an iron powder alloy.

L. S. BUSCH.—When intentionally adding impurities such as a stearate to copper-alloy powders, we found that before the piece started to shrink it expanded a very measurable amount. If we were careful how fast we heated the piece, we could prevent shrinkage and it would stay at the expanded height. If we heated

* See this volume, p. 402.

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it slowly enough, it expanded and then shrank. We were using induction heating to do this. You could actually see this happen.

GEORGE STERN.*—Dr. Rhines, it appears to me that a metallographic method for evaluating shrinkage of pores would involve some technical difficulty during the preparation of the sample. It is well known, for instance, that during polishing the pores can easily become enlarged and exaggerated in size and shape. I am referring to the homogeneous one-metal system specified by you. Could the modulus of elasticity be used as a measure of the rate of shrinkage of pores in powdered-metal compacts? It has been fairly well demonstrated that the modulus of elasticity for grey cast iron is a function of the size and shape of graphite pores. Would it not be possible, therefore, to measure the modulus of elasticity of powdered-metal compacts and relate the values obtained to the size of the pores appearing in the powdered-metal sample? In other words, might not such a quantitative method be used to parallel the study on the metallographic size of pores?

F. N. RHINES.—That is a nice suggestion. It occurs to me that another property that is pretty sensitive to porosity is elongation.

GEORGE STERN.—Yes, and perhaps reduction in area could be used as well.

C. G. GOETZEL.†—Has anyone observed any expansion on loosely heaped powder? That may throw some light on the question whether evolution of air entrapped during compaction is mainly responsible for the expansion, or some dissolved gases or residual stresses in the individual particles of the powder prior to the pressing operation.

F. N. RHINES.—I do not remember who it was—it may have been Miss Delisle—but someone commented that after long sintering of loose powders they sometimes expand again, presumably owing to the release of gases inside.

L. DELISLE.‡—In heating loose iron powders, the density of the cooled samples does not

continuously increase with the sintering temperature. As we pass the alpha-gamma transformation temperature, an expansion takes place. This phenomenon, which seems connected with the allotropic change, has been observed by many research workers. According to Schlecht, Schubardt and Duftschmid,* such an expansion is due to the breaking of the weaker bonds in the iron compacts as recrystallization takes place. The pressure exerted by entrapped gases may become more effective as the bonding forces are somewhat loosened in the course of the crystalline rearrangement.

Kalischer† made a study of dimensional changes of compacts made of different metal powders upon heating, but although he mentions the decomposition of oxides as a factor affecting the direction of the dimensional changes on the compacts, he does not draw definite conclusions.

T. C. WILSON.‡—I wonder if an investigation of the way in which sintering times vary with temperature would offer a better understanding of the process or mechanism occurring. For example, if the times needed at various temperatures to reach equivalent sintered products varied in the same way as they do in known diffusion processes, there would be some evidence that diffusion is one of the principal factors in sintering.

I believe Dr. Mehl did some work in an analogous fashion in investigating the times at different temperatures required to produce from cold-worked material equivalent recrystallized aluminum specimens. He found, I believe, the time-temperature relations similar to those found in diffusion experiments.

F. N. RHINES.—I agree with you. I intended to say pretty much the same thing.

H. W. HIGHRIER.§—I would like to add my word of commendation to Dr. Rhines for

* L. Schlecht, W. Schubardt and F. Duftschmid: Conversion of Carbonyl Iron Powder into Compact Pieces by Heat and Pressure. *Ztsch. Elektrochemie* (1931) 37, 485-491.

† P. R. Kalischer: The Effect of Particle Size on the Shrinkage of Metal Compacts, Symposium on Powder Metallurgy, Amer. Soc. Test. Mat. (March 3, 1943).

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his very fine summary, with which I can find no argument. It seems to me, however, that one point worthy of consideration has been overlooked. Considering the matter of sintering, we are concerned with forces and their effects at the contacts of particles. It seems almost inevitable that in the great majority of cases the individual powder particles that are in contact have different crystal orientations.

In the manufacture of some types of photo-cells, metals are often evaporated onto structures made of dissimilar metal, and the crystal structure differs from that of the common

structure of the evaporated metal. In such cases, the deposited film frequently will assume the grain structure of the material upon which it is deposited for a depth of several lattice parameters, even though in so doing it is assuming a grain structure foreign to its nature and involving considerable instability.

I wonder if in the points of contact between grains of different orientation that occur during sintering there may be a somewhat similar phenomenon, and the extreme lattice distortion that occurs near the grain boundaries may not help to propagate grain growth.

The Pressing Operation in the Fabrication of Articles by Powder Metallurgy

BY RICHARD P. SEELIG* AND JOHN WULFF,† MEMBERS A.I.M.E.

(Chicago Meeting, February 1946)

THE importance of the pressing operation in the forming of articles by powder metallurgy depends to a great extent on the type of product to be made. While in some few cases the pressing is merely a means of compacting loose powder particles into a solid mass preliminary to a sintering treatment, in most applications it constitutes a molding operation with the purpose of shaping the raw material in powder form into a certain predetermined, accurately defined part not altered in shape by subsequent sintering. In still other cases, no pressing at all but sintering in molds gives useful articles. A limited number of products are made by the simultaneous application of pressure and heat.

The factors that control the product of the pressing operation are raw material, lubricant, type, size and shape of die and compact, magnitude and time of application of pressure, as well as temperature of pressing. All such factors need to be controlled; yet, depending on the function of the pressing operation, greater emphasis may be placed on processing factors other than the pressing operation. In any complete discussion of pressing, subsequent sintering cannot be disregarded. For the sake of brevity, the present paper has been limited to the mechanics of pressing and only occasionally refers to sintering.

Manuscript received at the office of the Institute April 25, 1946. Issued as T.P. 2044 in METALS TECHNOLOGY, August 1946.

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For the same reason, hot-pressing has been omitted as beyond the scope of this paper.

In any survey of the literature on the pressing of metal powders, the 1938 paper of Balshin¹ on the theory of the process of pressing deserves mention.

The first attempts at an interpretation of pressing phenomena were made by Balshin¹ and Rakovski.² The experimental results of both are of great interest. Since the experimental results are not described, the work was repeated, using our own interpretation of the possible techniques, and is reported in the following pages. The basic theory of Balshin,¹ based on a hydrodynamic analogy, however, leads to but another way of plotting density and pressure against height of a pressed compact. Since it does not give any new insight into the phenomena, nor account for the influence of side-wall friction, a discussion of the theory has been omitted from this paper.

DENSITY GRADIENTS IN COMPACTS

The process of pressing metal powders in a die (disregarding for this consideration the powder filling and ejection operations) may be divided into three phases: (1) packing, (2) elastic and plastic deformation, (3) cold-working with or without fragmentation. It must be emphasized that these three steps do not follow each other in sequence; on the contrary, in practice

¹ M. Y. Balshin: Contribution to the Theory of the Powder Metallurgical Processes. *Metallpromisklennosti* (1938) 18 (2), 124-147.

² V. S. Rakovski: Fundamental Considerations in the Production of Hard Alloys. *Onit*. Moscow (1935).

the three phenomena usually overlap each other, and at least one of them may be absent under many conditions. For instance, in some cases, the powder nearest

were made of glass and the bottom and side walls of wood. The top punch, not shown in the figure, was also made of wood. The celluloid disks of three different diam-

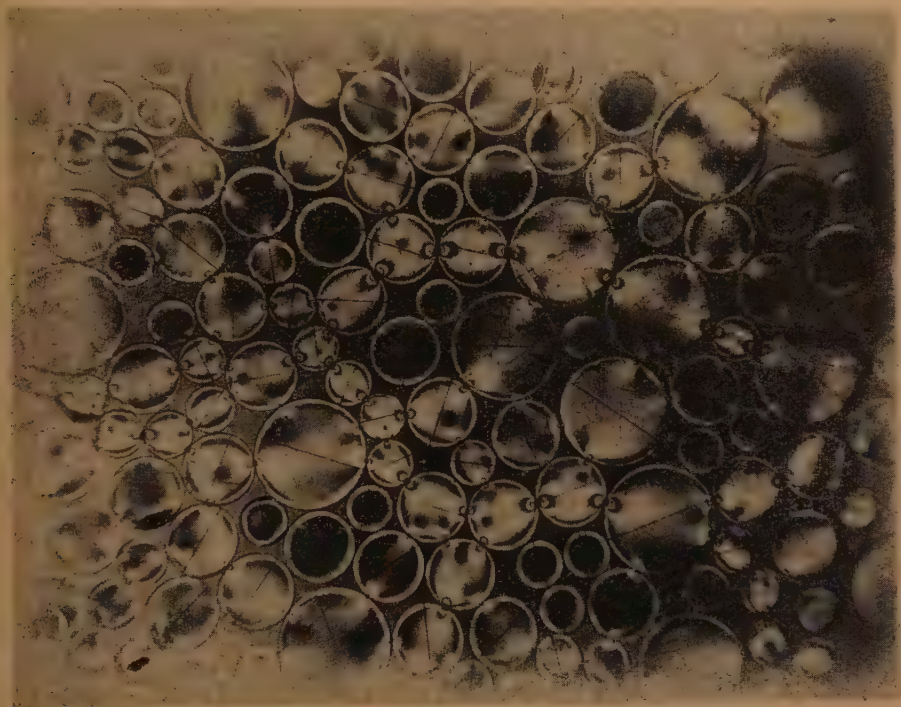


FIG. 1.—STAGES ONE AND TWO IN PRESSING METAL POWDERS IN A DIE.

the movable plunger may be in the third stage when the most distant powder is still in the first stage of pressing. With some powders, such as lead and tin, stages one and three are of little significance, and with very hard powders, such as tungsten carbide and chromium, plastic deformation is practically absent. Thus, the significance of any of the three phases depends to a large extent on the plasticity of the powder used.

Fig. 1, obtained by R. W. Vose at the Massachusetts Institute of Technology, using the technique of photoelasticity, illustrates stages one and two. Small flat disks of celluloid were pressed in a thin die of which the front and back walls

were dropped into the cavity, the die was vibrated to permit them to settle, and then pressure was applied by means of the wooden punch. The disks were photographed while under pressure, using polarized light. The first conclusion that can be drawn from this picture is that many voids or "bridges" are left between the particles. The illustration also indicates that some of the particles, particularly the small ones, are not even elastically stressed as a result of "bridging." If this were undeformable powder, such as tungsten carbide, the addition of a certain percentage of extremely fine particles would permit the feed of an increased amount of powder into the die cavity,

and thus a more effective utilization of the die space as well as an increase in the number and area of contacts between the particles. Any further increase in packing

was determined. From these findings, a plot was made of density versus height of the compact (Fig. 2), which shows that the density nearest the movable punch is

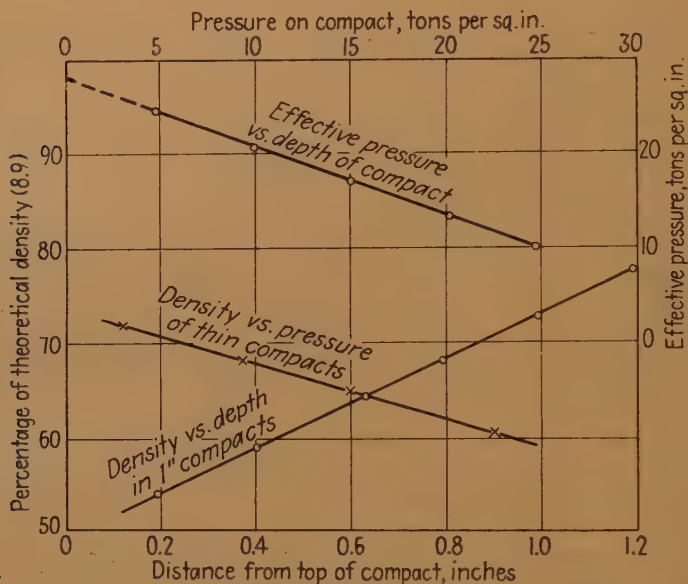


FIG. 2.—DENSITY AND EFFECTIVE PRESSURE IN GREEN NICKEL COMPACTS.

with such hard powders can be achieved only by fragmentation. On the other hand, if the powder were soft iron or copper, it is obvious that further densification could be accomplished by using a higher pressure, resulting in further plastic deformation. For the softer powders, then, an addition of extremely fine particles is not imperative in order to obtain improved density by pressing. From the standpoint of sintering, however, the addition of fine particles might prove more effective.

In order to follow experimentally what happens in the second stage of pressing, a compact 1 in. high and 1 sq. in. in cross section was pressed at 30 tons per sq. in. from one side only. The powder used was annealed electrolytic nickel powder. After removal from the die the compact was carefully cut into eight sections of equal thickness, and the density of each section

approximately 72 per cent, while at the opposite end it has dropped to 61 per cent of the absolute density of nickel. The fact that the density of the compact decreases from one end to the other means, of course, that the effective pressure on the powder layers near the punch is high, whereas it is much lower the farther the powder is removed from the punch exerting the compacting pressure. In order to illustrate the effective pressure drop in the compact, thin compacts approximately $\frac{1}{8}$ in. thick were pressed under various pressures. The resulting density values for each compact were determined. From the results plotted, a third plot can be made showing the change of the effective pressure with depth in a 1-in. compact. The third curve shows that when a pressure of 30 tons per sq. in. is used to compact the particular nickel powder involved, the effective pres-

sure of compaction near the bottom of a 1-in. compact is approximately 10 tons per square inch.

The densities plotted in Fig. 2 refer only to average density. By carefully cutting sections from the center and from the sides of slices of the compact, it was found that for low and intermediate pressures, about 15 to 40 tons per sq. in. for iron, a horizontal density gradient also exists. In the top sections of the compact the center is of lower density than the material near the side walls; in the sections at the bottom of the compact, the densities are reversed. This may be attributed to die wall friction.

Balshin¹ considers interparticle friction to be chiefly responsible for the density gradient met with in pressing. By mixing 4 per cent of graphite powder with copper, he finds that the density gradient can be practically eliminated. This experiment was repeated with nickel powder, using a pressure of 30 tons per sq. in. to obtain a compact 1 in. in diameter and approxi-

mately 1 in. high. The experimental results are given in Table 1.

For comparison's sake, one mix containing 4.5 per cent silica flour was compacted to 1-in. height and one straight nickel mix without lubrication but only to $\frac{1}{8}$ in. height, both at 30 tons. The density achieved with stearic acid in the mix, or only on the die walls in the pressing of 1 in. high compact is the same and equivalent to the density obtained in pressing a $\frac{1}{8}$ -in. high compact at the same pressure. In each case, the absolute density used for calculation was that for metal powder plus admix. Repeat measurements using 4 per cent graphite of an extremely fine particle size indicated that the measurable difference in density was real. As a consequence we cannot rule out interparticle friction; yet, it is apparent that die-wall friction is the factor of major importance.

Although used by Balshin¹ to illustrate density gradients, the technique of Rakovski² can also be used to illustrate die-wall friction. These workers use either metal foil or slight amounts of graphite powder to separate layers of equivalent weight of a metal powder in a die. After pressing a compact from such a multiple fill, it is possible to separate the individual layers for examination. The heights of each layer clearly indicate the lower density of the layers farthest removed from the punch. We have repeated these experiments using iron powder layers separated by a thin film of ultrafine copper powder. After compaction and ejection self-sustaining layers were separated with a razor blade. The lower surface of the layer nearest the movable punch always exhibits the greatest curvature. If the die walls are poorly lapped, the curvature is greatest in the section immediately adjacent to the die. The results are schematically given in Fig. 3. When the die walls are carefully lapped and lubricated and the compact height is not greater than the diameter, the layers are of

TABLE 1.—*Effect of Lubricants on Green Density of Compacts Pressed at 30 Tons per Square Inch from Nickel Powder*

MATERIAL AND TREATMENT	ABSOLUTE DENSITY, PER CENT
Nickel powder.....	66
Nickel powder + $\frac{1}{2}$ per cent graphite.....	76
Nickel powder + 4 per cent graphite.....	78
Nickel powder + 4.5 per cent silica flour.....	64
Nickel powder + 0.5 per cent stearic acid.....	75
Nickel powder; die walls lubricated with stearic acid.....	76
Nickel powder; die walls lubricated with colloidal graphite.....	74
Nickel powder—die walls lubricated with stearic acid.....	76
(This compact was $\frac{1}{8}$ in. high; all others were 1 in.)	

equivalent height and the parting surfaces are practically flat.

The relative importance of die-wall friction in introducing density gradients,

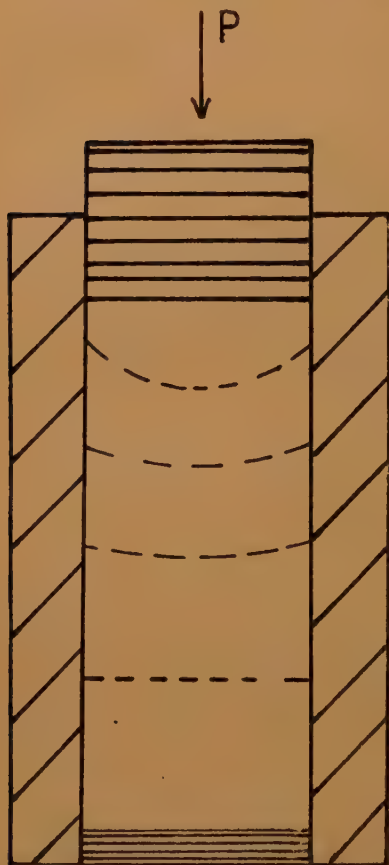


FIG. 3.—CROSS SECTION OF IRON POWDER COMPACTS PRESSED AT 80 TONS PER SQUARE INCH.

Curved surfaces delineated with copper powder using modification of the Rakovski method. Same experiment with a poorly finished die exhibited added curvature near die wall. Each powder section is of equal weight. Density of each section is inversely proportional to the area.

and thus stress gradients, depends also on the geometry of the compact and the pressure employed in compaction. In cylindrical compacts whose height is small as compared with the diameter, the frictional effect of the die walls is of lesser

importance. For each pressure used we have found with thin compacts that there is an optimum height of compact for maximum average density. Thinner compacts expand on ejection from the die because of the release of elastic stresses. Balshin¹ indicated this with tungsten and we have verified it with nickel and iron. As the height of the compact is increased to sizes greater than the optimum discussed, the density gradient in the compact becomes steeper for the same applied pressure. For a compact height which is about twice the diameter (and for constant height) the density increases with increasing pressure; yet the density gradient often becomes steeper only to flatten out again if extremes of pressure are applied. For hard powders, such as chromium and tungsten cracking occurs before the last stage is reached; for soft powders, such as lead and tin, such variation of the density gradient can readily be ascertained. With fully annealed iron and nickel powders, the last stage is not readily measured when the ratio of the height to diameter exceeds 3 to 1.

EFFECT OF RAW MATERIAL ON PRESSING IN PRODUCTION WORK

One of the most important factors in commercial pressing is the selection of the raw material itself. While it is a relatively simple matter to distinguish between the pressing behavior of copper and chromium powder, it is more difficult to differentiate between one type of iron powder and another simply on chemical composition and particle-size distribution.

With some materials humidity control is imperative if close final dimension control is required. Intentionally added impurities, such as corrosion inhibitors, if they are present in small amounts, are usually more beneficial than harmful. Nevertheless, all surface impurities, if they inhibit the formation of "cold welds" during pressing or "hot welds" during the sintering cycle, can be detrimental. A

particularly illustrative case is the lubrication of Alnico mixes with stearic acid. Too long a mixing time leads to compacts that have insufficient green or sinter

Fig. 4 shows two tensile specimens pressed from two different types of iron powder pressed at the same pressure. One shows a lamination crack failure; whereas, the



FIG. 4.—TENSILE SPECIMENS FROM TWO DIFFERENT IRON POWDERS PRESSED AT SAME PRESSURE.

strength. The use of the same amount of stearic acid in the mix, but less mixing time (less uniformity of coating) leads to the production of more acceptable products.

In most cases secondary constituents alloyed with the powder give harder powders, which are less readily compacted into intricate shapes in mass production schedules. Among intentionally used alloy powders, brass is quite amenable to pressing. For harder powders, the use of the proper fine particle-size distributions and the use of lubricant such as "Carbowax," "stearic acid" and other addition agents which function in part as adhesives are necessary.

The use of any particular powder in plant operations is often curtailed for certain applications necessitating high pressure, since lamination cracks occur perpendicular to the direction of pressing.

other is free from such shortcomings. The former powder is found adequate, however, for most applications requiring lower pressure. To be sure, the first powder can be somewhat improved by further annealing, but with the use of higher and higher pressures in the pressing of a powder slight differences in internal structure and chemical composition play a decisive role.

Such properties as compactability and green strength of various metal powders have not yet been standardized as to terms or tests. They are indeed difficult to define and standardization is all the more difficult because different manufacturers do not always agree on their performances, depending on the particular techniques used in their plants or the desired characteristics in their final products. Important features for the production man are:

1. The maintenance of sharp corners in handling green compacts.
2. Good definition of shape details.
3. Smooth surface.
4. Ability of powder to flow into small openings in the die cavity.
5. Ability of green parts to resist deformation or cracking where intricate shapes are handled and where density gradients cannot be avoided.

PRESS EQUIPMENT

Besides the capacity, the speed and method of operation (mechanical or hydraulic), there are many other functional differences between different types of presses usable for pressing metal powders.

It is in general recognized that where presses of more than 150 tons capacity are needed, hydraulic equipment is superior to other types. It has often been said that the press capacity imposes a limitation on the size of the parts that can be molded by powder metallurgy. This is not so. There are presses available, which were used in the aircraft and allied industries, of exceptionally high capacities. Such presses can readily be built or converted for use in powder metallurgy. The limitations are to be found elsewhere; mainly in the cost factor resulting from the operation of a large press, the building and maintenance of large dies, and the expense resulting from the subsequent sintering operations of large compacts as well as the cost of the powder.

The press builder is concerned not only with the total capacity of a molding press but also with the entire cycle. Specifically, he must know at what point of the cycle the press must exert most of the pressure and at what other points much lower pressures, or no pressure, must be exerted. Such knowledge enables the builder of hydraulic presses to design a machine with a rapid approach of the ram up to the last point of squeeze, and it enables the builder of mechanical machines to design

cams and levers in such a way that they are capable of carrying the full load when needed, with no unnecessary weight to be moved around during the remainder of the cycle. In order to investigate the pressure cycle more closely, small bars have been compacted measuring 1 by $\frac{1}{4}$ in. with a depth of cell of 0.750 in. Two materials were used; namely, copper B as furnished by Charles Hardy, Inc., and minus 100-mesh annealed electrolytic iron as furnished by Plastic Metals, Inc. Pressures ranging from 10 to 70 tons per sq. in. were used, and the thickness was measured after each compression. The values shown in Table 2 are averages of nine measurements of copper and six measurements of iron.

TABLE 2.—Measurements after Compression

Pressure, Tons per Sq. In.	Average Thickness, In.	Travel, Per Cent	Ratio
COPPER			
10	0.333	0.417	2.28
20	0.286	0.464	2.62
30	0.262	0.488	2.87
40	0.263	0.487	3.04
50	0.237	0.513	3.17
60	0.233	0.517	3.22
70	0.233	0.517	3.22
IRON			
10	0.322	0.428	2.33
20	0.281	0.469	2.68
30	0.263	0.487	2.85
40	0.251	0.499	2.99
50	0.245	0.505	3.07
60	0.235	0.515	3.19
70	0.232	0.518	3.24

The conclusion to be drawn from this table is that substantial pressures need to be exerted only near the very end of the compression cycle. Thus, the designer can plan on using not only the clearance between the punch and die, but also substantial travel inside the die, for a fast approach or for light structural design. An exception to this statement may be taken by some who have found by experience that a too fast entry of the upper punch into the die cavity results in ex-

cessive loss of powder, especially with worn dies or punches. This may be particularly annoying if powder is blown out of the cavity only at one or two points,

maximum pressure is exerted by the time merely 20 per cent of the vertical movement has yet to be traveled.

In the pressing of large flat parts, such

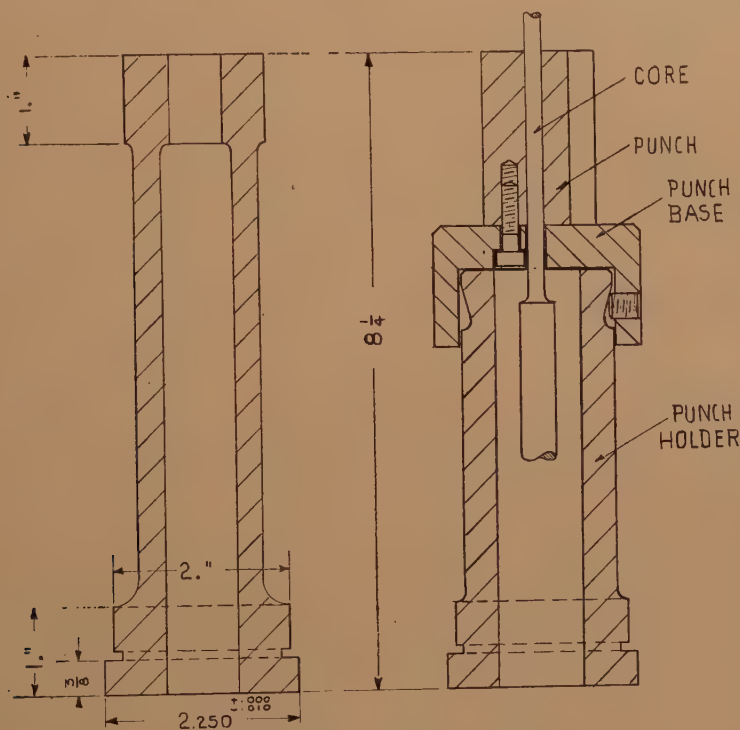


FIG. 5.—PUNCH AND PUNCH ASSEMBLY.
a. Lower punch as specified by press.

which may cause weakening of the structure of the part being made without obvious visible defects. However, particularly for the manufacture of parts requiring great depths of fill, these findings should be of interest. According to the tabulated data, the punch penetrated into the die approximately $\frac{1}{2}$ in. under pressure of 70 tons per sq. in. when the depth of fill was $\frac{3}{4}$ in. This penetration at maximum pressure may be called 100 per cent travel. Under the lowest pressure used (10 tons per sq. in.), the punch entered the die more than 0.4 in. for both materials tried. That is more than 80 per cent of full travel. In other words, less than 15 per cent of

as clutch facings or brake linings, very large presses up to about 1500 tons capacity are used. In one design of the ejection mechanism the compact remains under pressure for a short period after ejection from the die. Cracks due to ejection are reduced in this fashion.

Presses with more involved mechanism and more complex movements have become available during the past few years. Some of these are usable for one particular job and it is difficult to change to other types of parts. Others are quite flexible, but result in rapid wear on the drive mechanisms, such as cams, cam rollers and bearings. Still others prefer to use

relatively simple press movements and obtain the varied punch movements by means of intricate punches designed for each die.

hand design is substantially as specified by the press manufacturer. The one on the right side is a redesigned punch assembly resulting in the same over-all

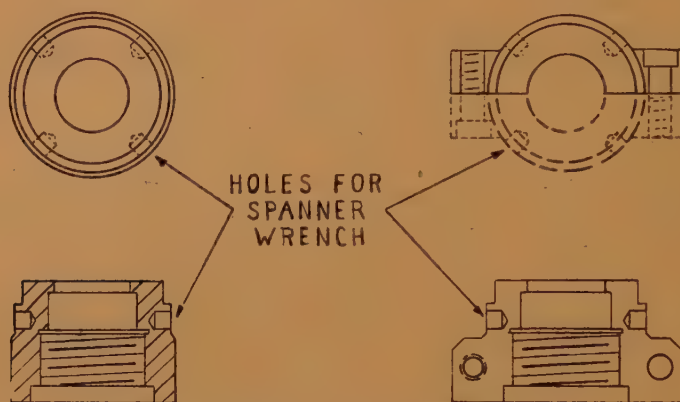


FIG. 6.—CLAMP NUT FOR LOWER PUNCH HOLDER.

- a. As furnished with machine.
b. Split nut, as used in production.

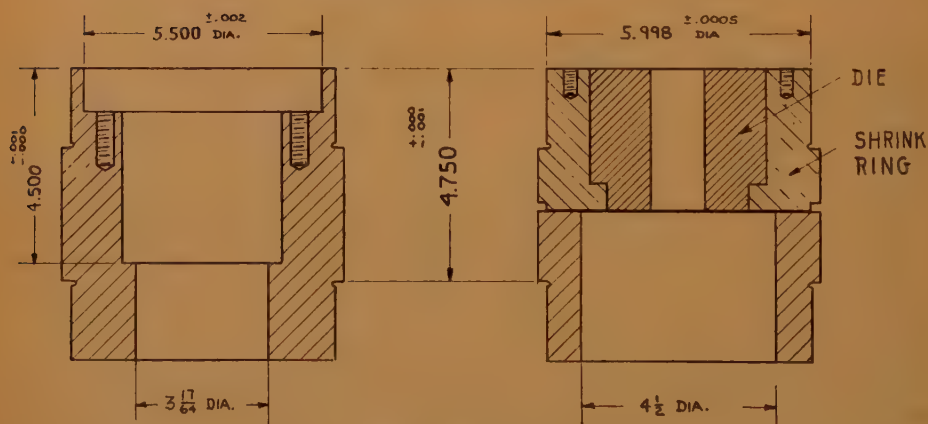


FIG. 7.—DIE HOLDER, DIE AND ADAPTER.

- a. Die holder, suitable for inserting dies of various heights but limited in diameter.
b. Die and adapter, designed especially for ease of assembly and setting.

The successful operation of a press often depends on details such as the design of adapters and holders for dies and punches.

Figs. 5 to 7 show a few typical examples of such designs. Fig. 5 shows a lower punch as used in a conventional mechanical compacting press. The left-

dimensions for proper timing of the cycle, but breaking the punch down into various components so that punches and cores can be easily assembled, aligned and replaced.

This punch is usually attached to the ram of the press by means of a clamp nut (Fig. 6, left side). By redesigning it as

shown at the right side, the assembly can be made much more readily, particularly when punches and die have to be set up as a unit. In other words, an assembly that is too large to fit through the opening of the single clamp nut can be set in to the press and then the split nut assembled around it before the punch is fastened.

Fig. 7 illustrates a design change in a die holder suitable for dies of limited depth, but allowing space for die shoes or shrink rings and permitting easy setting and disassembling. Some of the minor but helpful features include the small undercut between the die shoe and the die spacer, which permits the insertion of pry bars to lift the die out of the die table. The tapholes in the top of the shrink ring are provided also for the purpose of ease in removing the die from the press. This feature is important because in automatic operations the die must be level and flush with the die table in order to permit the feed shoe to slide freely across the surface, to fill the die cavity and remove the ejected part from the previous cycle.

The method of feeding the metal powder into the die is an important feature if control of dimensions and properties is important. On large and intricate parts, the feeding is often done by hand, and the human element is predominant. On smaller and simpler parts, the feeding is often mechanized and sometimes is completely automatic. Regardless of whether the feeding is manual or mechanical, one of two methods is used—by bulk or by weight. The choice is more often dictated by convenience.

In order to determine the effect of the method of feeding the powder on the consistency of sizes in the pressed as well as sintered compact, experiments were run on both hydraulic and mechanical presses. At the same time, the effect of the method used in reversing the press ram was also studied. Table 3 shows the

conditions of the first group of experiments made on a hydraulic press.

TABLE 3.—Conditions of First Group of Experiments on Hydraulic Press

Batch No.	Method of Feeding	Method of Reversal	Approx. Pressure Tons per Sq. In.	Results
1	Bulk	Stroke	10	Size variations relatively low Size variation relatively high. Weight more consistent than in batch 1 Relation between batches 3 and 4 similar to that for lower pressures When powder is fed by weight, the method of reversal of the ram has no appreciable effect on size
2	Bulk	Pressure	10	
3	Bulk	Stroke	30	
4	Bulk	Pressure	30	
5	Weight	Stroke	30	
6	Weight	Pressure	30	

From the experiments described, it becomes clear that the green sizes are more accurate if the press is reversed by stroke. However, no greater consistency in weight of compacts can be accomplished by this method. There is a tendency toward greater variation for the lower pressures employed. Greater accuracy in size, and, of course, also in weight can be accomplished only by batch weighing the powder charge. Sintering of the samples used in these pressing experiments shows that the trend after sintering follows fairly closely that established for the green pieces.

On a mechanical press, the method of reversal cannot usually be varied. Therefore, only the three following conditions were studied:

1. Manual powder feed by bulk.
2. Mechanical powder feed by bulk.
3. Manual powder feed by weight.

The difference between size stability for the various methods was not as great as anticipated. The main advantage of mechanical over manual bulk feed con-

sisted in eliminating occasional considerable deviations resulting from the human element. The average results, however, were fairly close. The main advantage of weighing the powder for a mechanical press seems to become apparent only when a repressing operation after sintering is required. In this case, much greater size accuracy can be maintained after coining because the same amount of metal is available in each blank.

DIES

Unfortunately, there is no universal answer to the question regarding selection of proper die materials because production conditions vary widely. Die materials must be selected according to the number of pieces to be produced, the pressure to be applied and the material in hand. Other factors, also, need consideration, even though they are not directly connected with service requirements, such as deformation in heat-treatment, machin-

ability, or other attribute. The guiding principle in most cases is hardness for wear and toughness for pressure. Table 4 gives a list of die materials in common use.

Additional advantages gained from the use of such materials as high-carbon, high-chromium steels, tungsten carbide, and the use of chromium plating result from the fact that they exhibit relatively low coefficient of friction at high pressures when properly finished. As mentioned in the description of laboratory work, the loss of pressing energy in die-wall friction leads to disturbing density and stress gradients. The use of die materials that tend to reduce these effects is important, therefore, if their control is essential. Such surface treatments as plating or nitriding have the advantage that if dies wear, an application of such treatments may enable the producer to recondition the tool after it has worn beyond established tolerances.

Punches, cores, supports and auxiliary parts all have different functions to per-

TABLE 4.—*Die Materials in Common Use*

Production	Pressure	Die Materials			Treatment	Hardness, Rockwell C
		Code No.	Designation	Type Analysis, Per Cent		
Short or trial runs.....	Low	1,2,3	Kirkcaldie, cast iron, or bronze			
	Low High	4 5	Cold-rolled steel Oil-hardening tool steel	0.9 C, 1-1.5 Mn, 0.25 Si, 0.5 Cr, 0.5 W	Caseharden 1400°-1450°, oil quench; draw: 375°-400°	61-62
Medium run, 5M to 50M pieces	Low	5	Oil-hardening tool steel	Same as No. 5 above	Same as No. 5 above	61-62
	High	6	Nickel-chrome tool steel	0.75 C, 0.6 Mn, 0.25 Si, 1.4-1.7 Ni, 0.75 Cr	1500°-1550° oil quench, draw: 275°-300°	58-59
Long run, 50M to 500M pieces	Low	7	High-carbon, high-chrome	2.C, 0.3 Mn, 0.25 Si, 13 Cr, 0.2 V	1750°-1800° oil quench; draw: 400°	62-63
	High	7a	High-carbon, high-chrome	2.C, 0.3 Mn, 0.25 Si, 13 Cr, 0.2 V	1750°-1800° oil quench; draw: 800°; chrome plate	58-59
Very long run, 500M and over	Any	7, 7a	High-carbon, high-chrome	Same as No. 7 above	Same as No. 7, above; re-grinding or replating as needed	
	Any	8	Cemented carbide inserts			

form and experience teaches what steels and treatments are best in each case. For punches the selection is sometimes particularly difficult because they act not only as compression members but also as ejectors, and sometimes form part of the cavity. While ordinarily a tough steel, such as the nickel-chromium steel (code No. 6, Table 4) would be expected to resist repeated compression, occasional uneven pressure distribution, and some wear, owing to sliding motions through the die walls. A more wear-resisting material may be necessary where steps or depressions are formed in the punch, or compression actually takes place inside a multiple plunger. In extreme cases, surface hardening, plating or the use of carbide inserts is required.

SUMMARY

For the purpose of developing a theory of metal powder pressing and to demonstrate some of the phenomena that take place experimentally, it is convenient to consider the process as consisting of three phases. There is no definite demarcation or sequence between these phases:

1. Experiments described show the importance of suitable *particle-size distribution and the effect of bridging in the first phase, called packing. The chemical and mechanical nature of the particle surfaces affect the process. The energy applied to the powder mass is largely absorbed by interparticle friction.

2. The second phase of powder pressing requires as a necessary condition a certain amount of plasticity in the powder. It was possible to demonstrate by experimental work that a considerable amount of the applied energy is absorbed in die-wall friction, leading to highly undesirable density gradients. It was further possible to ascertain that in comparing interparticle and die-wall friction, the latter exerts the predominant effect. The remainder of the energy applied in the second phase of

pressing goes into interparticle friction and deformation of the particles.

3. In the third stage of pressing, which is characterized by the susceptibility of the powder particles to either cold-working or fragmentation, high residual stress may be induced in the compact. They lead to size changes and even failures after pressing, but they may be beneficial for the subsequent sintering operation.

For production purposes, powders react differently, depending on purity, particle size, size distribution, and shape, as well as on method of manufacture. Such properties as "compactability" and green strength are of great practical importance, but are not readily defined nor amenable to testing.

In connection with equipment used for production of pressed parts, the question of pressure distribution during a complete cycle of the press was studied. As expected, high pressures are needed only very shortly before maximum stroke is reached, allowing the rest of the travel to be used for rapid approach, and other effects. Another point of considerable practical importance, which needs to be neglected in a theoretical approach, is the effect of the method of feeding the powder and reversing the press ram (constant pressure vs. constant stroke) on the size of compacts in the direction of pressing. Experiments show that greater dimensional accuracy can often be produced by weighing the powder-charge. If bulk feed is used in a hydraulic machine, more consistent sizes can be obtained by reversing the ram at a predetermined stroke rather than by pressure.

A representative group of die materials for different quantity and pressure conditions has been compiled. The general principle in selection of die material is: hardness for wear and toughness for pressure. Friction characteristics under pressure are also important. Emphasis must be put, therefore, also on the heat-treatment or surface treatment. The

requirements for punches, cores and auxiliary parts are quite different, so that different materials and treatments are usually selected.

ACKNOWLEDGMENTS

The authors wish to thank Mr. R. Kamm and Mr. M. Steinberg, graduate students at M.I.T., who carried out the density measurements; as well as Mr. C. E. Tarpley and Dr. B. P. Planner, at Powder Metallurgy Corporation, who performed size-control and pressure-cycle experiments reported in this paper.

DISCUSSION

(*R. P. Koehring presiding*)

A. SQUIRE.*—This is a most interesting paper and some data in it are corroborated by work I did at Watertown Arsenal some time ago with iron powder. I would like to ask Dr Wulff to say just a little more about the compressive and tensile stresses on the surface of compacts.

JOHN WULFF (author's reply).—Our work has not yet been completed; although enough data have been obtained with cylindrical compacts of iron to permit some conclusions. Briefly, in a compact $\frac{3}{4}$ in. high and $\frac{1}{2}$ in. in diameter pressed at 48 tons per sq. in., the residual stresses on the surface measured by X-ray diffraction techniques are as follows:

The radial stresses on top center and bottom of compacts are practically zero; the longitudinal residual stresses on the side walls are near the top quarter of the compact about seven tenths that of the yield point of mild steel in tension; at the center surface of the compact they are in compression and in magnitude about 0.3 that of mild steel in tension; near the bottom, they are practically zero.

F. V. LENEL.†—I was particularly interested in the work that Messrs. Wulff and Seelig reported on the influence of lubrication

on the density of parts. In connection with the work of the American Society for Testing Materials on determining the green density of a compact, we ran into considerable difficulty in getting reproducible results of green-density determinations. It was much easier to get a reproducible green density when the lubricant was mixed with the powder than when the lubricant was applied to the die walls; particularly when the die was not perfect—i.e., if it was somewhat rough or out of round. In this case, it was almost impossible to get reproducible green densities when the die walls were lubricated, while it was not too difficult to get reproducible results when the lubricant was mixed with powder.

JOHN WULFF.—Unless the lubricant is applied to the die wall as a slurry, and allowed to dry first or remain in place during the powder filling of the die, it is too often wiped away. This may account for the lack of reproducibility of Dr. Lenel's results. That better reproducibility is obtained by mixing the lubricant with the powder can only be explained by the fact that lubricant is extruded from the powder on the die walls during pressing. In any case, a poorly finished die introduces such a high friction that even lubrication does not make for more uniform distribution of density.

GEORGE STERN.*—This whole question of lubrication in powder metallurgy is highly interesting from both the theoretical and practical point of view. It has been pointed out that a good green density can be obtained just by painting the die wall, and that no improvement is brought about by mixing the lubricant with the powder prior to pressing. This takes into account only the pressing of metal powder.

Then the question of sintering enters into the picture. Many hold to the belief that in introducing an internal lubricant we are merely introducing an impurity, which will prevent the sintering action. We take a pure chemical powder (for which we paid a premium price) and deliberately contaminate it with an impurity, namely an internal lubricant. This

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question has arisen many times in our own organization. It would be extremely worth while if someone could devise a method for automatically painting the die wall and thus eliminate the introduction of a contaminant into the powders. Until such time, I am afraid we will have to go along with our "primitive" methods of blending impurities with powders and introducing trouble during sintering because we have no means of painting die walls mechanically in our commercial presses.

JOHN WULFE.—Mr. Stern has aptly stated the practical case of lubrication in powder metallurgy. What I have to say is but an addition to his remarks. In the pressing of Alnico mixes, it can be shown that with some lubricants applied dry, it is possible to coat completely each particle with a film, which during sintering leads to barriers that prevent sintering altogether. The same lubricant applied in less vigorous fashion—that is, in shorter mixing times—leads to complete diffusion alloying during sintering.

J. E. DRAPEAU, JR.*—Have you noted any effect of the rate of compressing metal powders on the density of the green compacts? (Rate of compressing might be considered as rate of cold-working of the powdered metal compact prior to sintering.)

JOHN WULFE.—We have not as yet found any significant differences in the average density of compacts pressed at different speeds. We need to explore the subject further; yet, we have noted two different types of cracks. In cases of slow pressing of hard powders, shear cracks at about 45° to the wall face appear; in rapid pressing, the cracks are of a more lamellar nature. Perhaps Mr. Drapeau refers, however, to thin compacts. In this

case Balshin showed for tungsten what we later found with nickel, copper and iron; namely, that for any pressure there appears to be an optimum thickness whose density is a maximum. Thicker and thinner compacts exhibit a lower average density. Higher pressing speed appears to shift this maximum. This work is as yet not completed.

(W. R. Toeplitz presiding)

C. G. GOETZEL.*—Tying in to some extent with the question raised by Mr. Drapeau concerning the rate at which pressure is applied, I should like to ask the authors whether they have ever considered the possibility of applying the pressure dynamically? There is some interest now in the problem of applying so-called "dynamic loading," particularly for very high pieces, and the ideas go in the direction of using a dynamic drop-hammer type of press, a percussion press, or a simple type of pneumatic drill press of the kind used in breaking asphalt in the street. The claims are—at least from one source—that friction effects on the die walls are very much changed by this kind of pressure. In fact, it is claimed that the friction is lessened at the die walls and that very high compacts can be pressed to a much greater uniformity in particle concentration by this method.

JOHN WULFE.—My answer to Dr. Goetzel's question is the same as that for Mr. Drapeau. I may add that some years ago we tried rapid pressing in a percussion press. The ram was activated by igniting an explosive mixture. Unless we introduced adhesives with hard materials, briquetting was extremely difficult. With metal powders it was difficult to avoid cracking of the compact, and with relatively soft powders, freezing.

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Pressing Complicated Shapes from Iron Powders

By CLAUS G. GOETZEL,* MEMBER A.I.M.E.

(Chicago Meeting, February 1946)

PRESSING of powdered metal parts is best done in the direction of the shortest extension of the piece, to avoid too great a loss of pressing force through internal

set forth here, are applied under the condition that presents the more difficult problem.

For clarity, before description of the

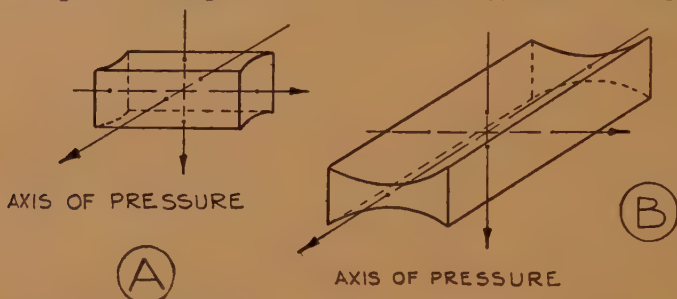


FIG. 1.—CHANGE IN CROSS SECTION UNDER PRESSURE.

friction. As long as curved surfaces, recesses, or offsets occur only parallel to this shortest axis of pressure, no special difficulties arise: the cross sections, perpendicular to the pressure, do not vary, nor does the shape of the parts change during compression except for a gradually reduced thickness (Fig. 1A). The problem becomes more difficult, however, when the curved surfaces or recesses are perpendicular to the shortest axis of the part (Fig. 1B).

Two processes for molding uniformly dense parts with complicated shapes from powdered metals are described in detail in this paper. Both can be employed successfully by those trained in the art. The first refers to curved parts; the second is especially adapted to parts having one or more recesses or steps. Both methods, as

two practical methods, the variable factors in molding powdered metal parts will be reviewed, then an idealized procedure will be considered briefly.

VARIABLE FACTORS IN MOLDING POWDERED METAL PARTS

Compression Ratio

Compression ratio is defined as the proportion of the final relative density of the compact to the apparent density of the powder. For iron powder of an apparent density of 3.0, for example, a compression ratio of $2\frac{1}{2}:1$ would be required to produce a compressed compact of 7.5 density; whereas for another iron powder having an apparent density of only 1.5, a compression ratio of 5:1 would be required to produce the same density. The lower the powder's apparent density, the greater must be the compression ratio for pressing compacts of high density.

Manuscript received at the office of the Institute Dec. 1, 1944. Issued as T.P. 1920 in METALS TECHNOLOGY, October 1945.

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Metal powders, manufactured by various methods, vary widely in their apparent densities, and the choice of a powder of satisfactory density is in practice governed

the compression ratio, the shorter the distance an average powder particle must travel during the compression of the powder from its loose state to its dense

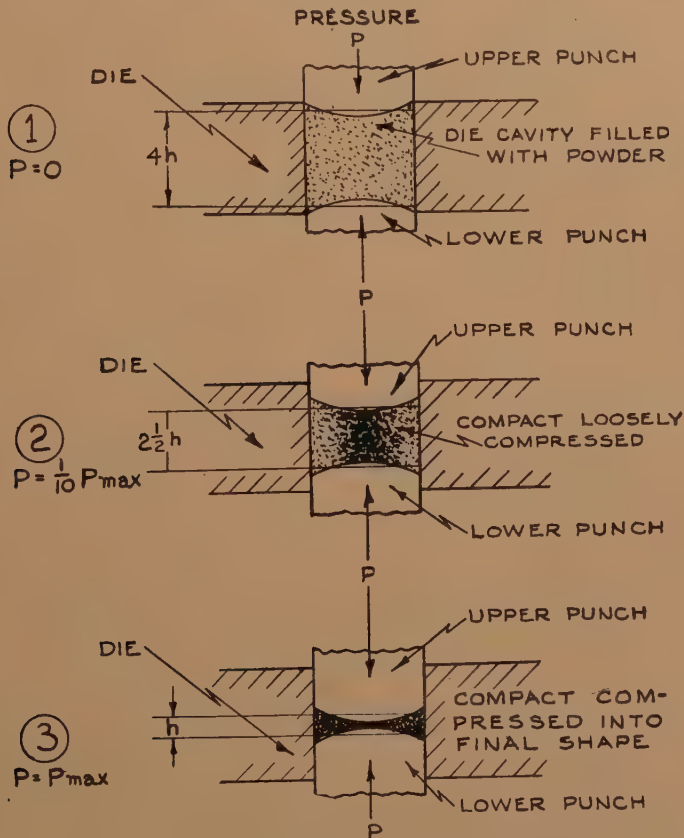



FIG. 2.—CONCENTRATION OF PARTICLES OF POWDER.

largely by conditions prevailing during molding. Powders of relatively high apparent densities (and consequently smaller compression ratio) are better adapted to quick-acting mechanical presses, since they flow more rapidly into the die cavity. Moreover, a shorter stroke of the press slides is required and the molding cycle is thus accelerated.

On the other hand, the use of such powders has an adverse effect on uniformity and cohesion in complicated shapes of the kind discussed here. The smaller

shape. Most of the particles would tend to travel only a short distance in a direction parallel to the axis of pressure, with little or no deflection in the direction demanded by the irregular contour of the body to be pressed. Consequently there result gross concentrations of powder particles in certain small cross sections, while other larger cross sections are substantially depleted (Fig. 2 and Table 1). The high concentration of particles in the thin cross sections produces some very dense areas with severely strained particles, often

TABLE I.—*Density of Pole Piece from Iron Powder (Apparent Density 1.88 Grams per Cubic Centimeter) Pressed Immediately into Final Shape*

Form	Density			Com- pres- sion Ratio ^a
	Section	Grams per C.C.	Per Cent of 7.87	
Final Shape	Overall	7.20	91.5	3.83:1
	A	6.63	84.2	3.53:1
	B	7.23	91.9	3.85:1
	C	7.75	98.5	4.12:1
	D	7.25	92.1	3.86:1
	E	6.68	84.9	3.55:1

^a This is the ratio of the relative density of the final compact to the apparent density of the powder.

showing planes of rupture, and other cross sections showing extensive porosity. Frequently, because of lack of sufficient material, sections with such loosely compacted particles crumble during ejection from the die or during handling thereafter.

Pressure

Each powder has its own limitations in the pressure range useful for molding. A narrow range of pressure applicable, as with refractory metal powders, may be disadvantageous, as it may require special presses for different powders and shapes. A wide pressure range, on the other hand, permits a better choice in the selection of presses and the use of any one press for a number of applications.

The lower limitation in pressure is fixed by the ability of the powder particles to adhere to each other when forming stable contacts in areas increased by plastic deformation of the particles. This lowest compacting pressure, at which the particles adhere and a compact with sharp outlines is formed, may be as low as $\frac{1}{2}$ ton per square inch for certain soft iron or copper powders, but it may also be as high as 50 tons per square inch for harder powders, such as steels. Certain very hard powders, such as hardened steels, may not be compressed at all at any feasible

pressures, say below 200 tons per square inch.

The upper limit of the pressure range is controlled by several factors—again by the particle plasticity, but also by the entrapment and compression of air, and by limitations imposed by press capacity and die strength. Soft and plastic powders tend to show particle overstraining and compacts thereof exhibit cone-shaped cleavage cracks above a certain pressure, usually above 100 to 150 tons per square inch. The maximum permissible pressure depends very much on the thickness of the thinnest cross section, and may be as low as 50 tons per square inch for very thin cross sections. For harder powders, this maximum pressure cannot be generalized, as it may be very high (for steels) or very low (for tungsten, molybdenum, etc.). Air entrapment usually cannot be prevented, and the highly compressed air tends to expand abruptly upon pressure release, ejection or subsequent sintering. Press capacity and die-strength limitations impose at present maxima of about 60 tons per square inch pressure for quick mechanical press operations, and 100 tons per square inch pressure for slower hydraulic press operations.

Particle Plasticity

The behavior of a powder under pressure is influenced by the softness and plasticity of the metal particles. Hard particles, such as steel or chromium, offer great resistance to compacting and deformation under pressure, and may only be compressible within a close range of comparatively high pressures or with the aid of plastic binders. Soft powders, such as copper or sponge iron, can be compressed to bodies of various densities by applying pressures in a wide range. At the same time, the degree of plasticity affects the ability of the particles to deform, to bypass each other or to move in a lateral direction. The softer the powder particles,

the more easily they can be moved to fill the voids and equalize the density.

Lubricants

Lubricants—usually powdered stearates, waxes, or similar materials—to which a commercial solvent has been added are mixed with the metal powders. Upon evaporation of the solvent, they form films around the metal particles and thus facilitate slippage of the particles past each other, closer packing of the mold cavity under a given pressure, and the shifting of particles from regions of high to those of lower concentration. During compression, part of the lubricant, oozing outward and covering the inner faces of the die cavity and punches, lessens abrasions of these faces and adherence of powder particles to them. Finally, by reducing flow disturbances and deformation of the particles in the surface layers, the lubricant produces compacts with smooth side faces.

IDEALIZED MOLDING OF UNIFORMLY DENSE COMPACTS WITH CURVED FACES

Uniformly dense compacts having large concave or convex faces in a plane parallel to the longitudinal axis can be molded best if the compression ratio is large and kept constant in each plane parallel to the axis of pressure throughout the entire compressing operation. This is illustrated in Fig. 3 for a concave body, and in Fig. 4 for a part with a convex face. The illustrations represent idealized cases for a compression ratio of 4:1. In order to maintain this compression ratio over the entire width, the powder of an apparent density of 1.8 could not be filled flush with the top face of the die. Instead, its top layer of particles would have to follow an elliptic curve, and the powder-fill volume would be strongly concave (Fig. 3) or convex (Fig. 4). This concavity or convexity of the ideal powder-fill curve could be only slightly reduced by having the

curved face of the final part placed downward (*B*) instead of upward (*A*).

If a truly iso-dense compact is the object, the compression ratio must be maintained uniformly throughout the entire cross section at every stage during the actual compression. If, for instance, slight pressure ($P = P_1$) from top to bottom results in one fourth densification of the powder, the compression ratio must change from the initial 4:1 ($P = P_0$) to 3:1 throughout the entire cross section. The initial curve of the top powder-particle layer would have to flatten out into another curve of larger parameter. This means that the top punch curvature would flatten with increased compaction to follow the changing powder curve; and also, that the individual particles would have to move only in planes (*A-A*, *B-B*, etc.) parallel to the axis of pressure, excluding any lateral movement. The same procedure would follow if the pressure were increased ($P = P_2$) until the maximum necessary to obtain the uniformly solid body was obtained.

In practice, this idealized molding procedure is not feasible, for several reasons: The shape of the top punch, if made from metal, cannot change during the pressing operation. The curved powder fill cannot be obtained in industrial press and molding equipment, all of which operates on a level powder fill, flush with the top face of the die. The idealized type of filling, moreover, would require complicated feeding devices, providing vibration, scraping, or other means for removing the excess powder. Finally, there is no way in which to prevent the individual powder particles from deflecting in a lateral direction, once pressure is applied. It may be said that during compaction the particles under pressure will follow the path of least resistance, which may not necessarily be the longitudinal direction. The movement of the particles is influenced mainly by such factors as interparticle friction, particle

shape, plasticity and work-hardening of the particles, configuration of the die cavity, type of lubricants, speed of pressing. A powder mass under pressure behaves

the method has given satisfactory results. A picture of such pole pieces in their different stages of production is shown in Fig. 5, and a drawing of one typical design

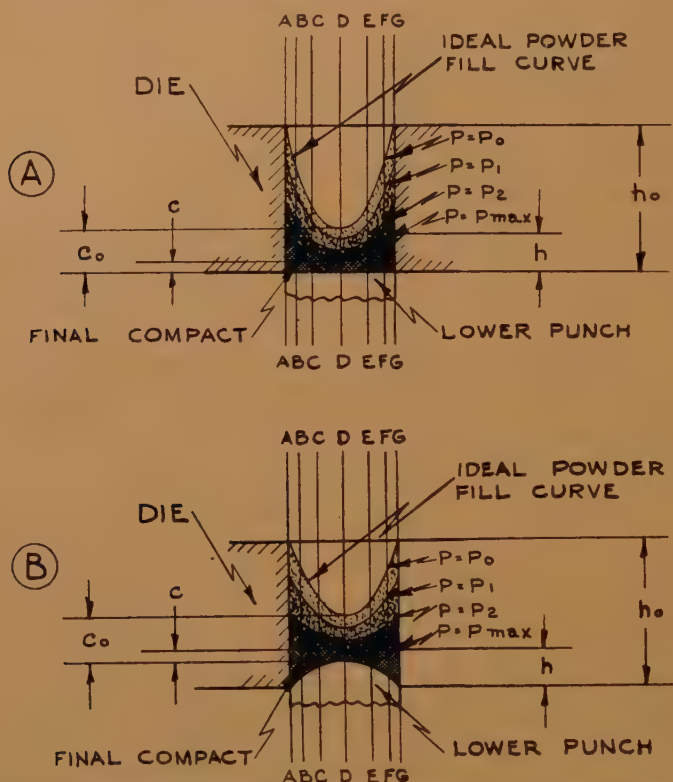


FIG. 3.—IDEALIZED CASE FOR COMPRESSION RATIO OF 4:1, CONCAVE BODY.

neither like a liquid nor like a solid, and the compact tends to absorb and transmit the pressure as though it were a brittle solid body only if high pressures are employed.

PRACTICAL METHOD OF MOLDING UNIFORMLY DENSE COMPACTS WITH CURVED FACES

A practical method of molding powders has been worked out which may be considered an approach to the idealized case. Applied on a mass production scale in molding generator pole pieces for field telephones from soft, spongy iron powder,

in Fig. 6. This field pole piece, mainly a flat, rectangular plate approximately 2 in. long, 1½ in. wide, and ⅜ in. thick, has, however, one large face curved with a radius of approximately ¾ inch.

By employing regular level feeding of the powder, the method of molding this shape enables us to use industrial molding equipment. The powder to be allotted for each compact is fed from a hopper into the die cavity, and leveled off flush with the top of the die face. As the die cavity and the position of the punches during loading are the same for each press cycle, this volumetric method of controlling

the amount of powder to be briquetted has been found accurate enough for all practical purposes. However, for extreme accuracy in the final dimensions of the

that could change its curved face during molding.

These needs have led to the introduction of a fractional molding, with inter-

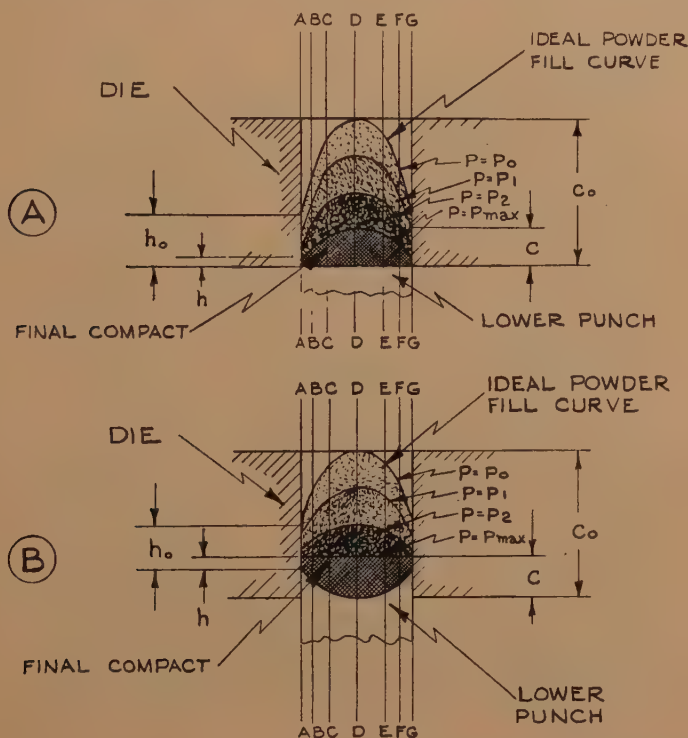


FIG. 4.—IDEALIZED CASE FOR COMPRESSION RATIO OF 4:1, CONVEX FACE.

compact, requiring variations in weight of less than 1 per cent, the batch-weight method has been used successfully. Here, each powder allotment may be weighed with the aid of a photocell-controlled exact weight scale, and then fed into the die cavity. No leveling of the powder flush with the die top is necessary; to prevent losses of powder that would upset the accurate weight method, the lower punch may even be set low enough to permit a powder-fill level slightly below the die-top face.

Two requirements therefore were to be met: (1) to assure that the compression ratio changes as desired during intermediate stages; (2) to provide a top punch

mediate heat-treatments, yielding partly compressed, porous bodies of shapes intermediate between the powder-fill shape and the final contours of the dense body. At the same time, favorable distribution of material in the intermediate compact was obtained by curving both the upper and lower faces as shown in Fig. 7. In the final pressing (coining) operation, the more shallow curvature is flattened out into a plane face.

The number of intermediate steps, and the configuration of the resultant intermediate shapes, were found to be dependent on several factors; namely, (1) degree of final density, (2) plasticity of powder particles, (3) tendency of particles to flow

under pressure and to by-pass each other, (4) use of lubricants, (5) radius of the curvature in the final compact, (6) conditions prevailing during intermediate sintering, (7) ductility of the metallic

compacts were pressed from two opposite directions in a single-movement press.

5. The porous intermediate bodies were heated at a temperature below 1100°C for at least 15 minutes.



FIG. 5.—POLE PIECES IN DIFFERENT STAGES OF PRODUCTION.

body after intermediate sintering, (8) type of pressing.

For the pole piece shown in Fig. 6, one intermediate shaping has been found sufficient to produce parts whose density averaged 93 per cent and did not vary more than ± 1.5 per cent throughout the cross section. To obtain these favorable results, however, the following conditions had to be fulfilled:

1. A very plastic iron powder of the reduced sponge-iron type was used.
2. To facilitate interparticle slippage, up to 1 per cent of a powdered vegetable stearate was added to the powder as a lubricant.
3. An intermediate porous body, curved on the two opposite sides, the porosity being about 50 per cent, was pressed first.
4. By means of a floating die setup, the

6. In order to render the compact ductile enough for the second pressing (coining), all impurities, such as oxygen or foreign matter introduced by the lubricant, were removed during a preliminary heat-treatment at a temperature below 700°C .

7. To remove effects of the severe strain-hardening after the second pressing, a heat-treatment at a temperature not lower than 800°C . was added. For certain products this second heat-treatment was carried out at temperatures above those necessary for the first.

As an intermediate shape, a body was formed whose one radius r_0 was $\frac{3}{4}$ of that of the radius r of the final piece; while the opposite curvature had the same radius r as the final piece. This design facilitated the pressing of a sufficiently porous body with considerable material pushed into the

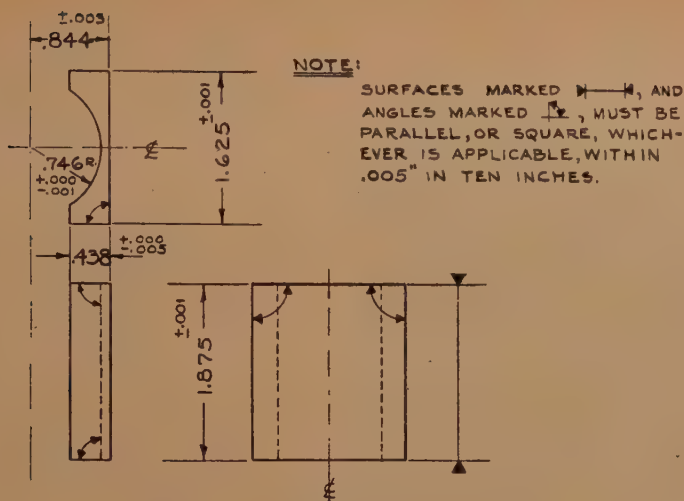


FIG. 6.—TYPICAL DESIGN OF POLE PIECE.

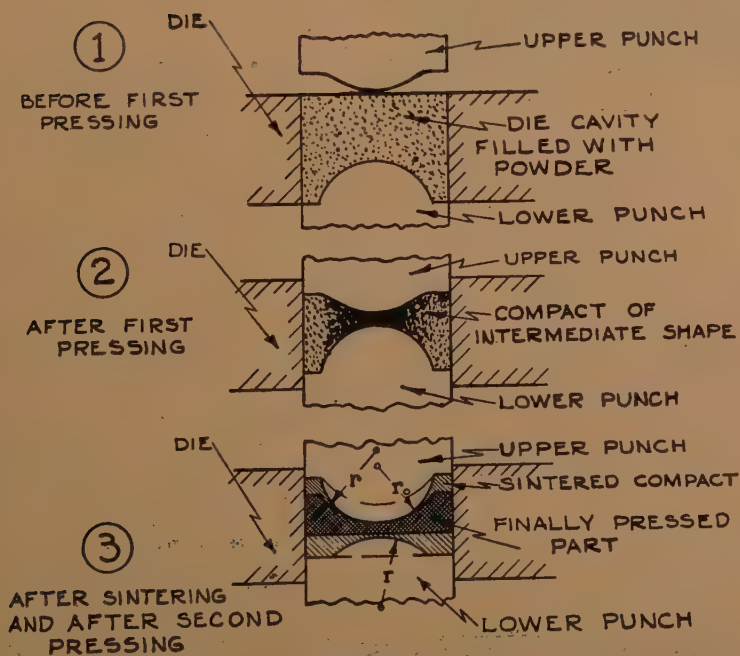


FIG. 7.—DISTRIBUTION OF MATERIAL IN INTERMEDIATE COMPACT OBTAINED BY CURVING FACES.

heavier side regions to allow coining into a practically iso-dense part approximately $\frac{5}{16}$ in. thick at the sides and $\frac{1}{16}$ in. thick in the center. For the first pressing, a



FIG. 8.—ARMATURES IN DIFFERENT STAGES OF MANUFACTURE.





pressure of 5 to 10 tons per square inch was found most suitable, as it yielded sufficiently strong compacts whose thinner center regions, though denser than the sides, were nevertheless not overstrained by excessive local pressure. On the other hand, a pressure of this magnitude formed bodies of approximately 50 per cent density, which, after sintering, were ductile and compressible enough to be coined into their final shape at pressures of 50 to 70 tons per square inch. Table 2 gives some data of compression ratios and densities in various sections of the preformed and final shapes.

PRACTICAL METHOD OF MOLDING UNIFORMLY DENSE COMPACTS WITH OFFSETS, STEPS AND RECESSES

In molding iso-dense parts having step-like projections, recesses or offsets, a

procedure similar to that outlined herein can be employed. Again, it must be borne in mind that such molded bodies will have a uniform density throughout only if, at every stage of the press operation, the

TABLE 2.—Density of Pole Pieces from Iron Powder (Apparent Density 1.88 Grams per Cubic Centimeter), Pressed First into Different Preforms, and Afterward Coined into Final Shape

Form	Density			Compression Ratio ^a
	Section	Grams per C.C.	Per Cent of 7.87	
Preform having final radius on both sides. 	Overall	4.04	51.3	2.15:1
	A'	3.71	47.1	1.97:1
	B'	4.18	53.1	2.22:1
	C'	5.26	66.9	2.80:1
	D'	4.23	53.8	2.25:1
	E'	3.77	47.9	2.00:1
Final Form thereof. ^a 	Overall	7.27	92.4	1.80:1
	A	7.07	89.9	1.89:1
	B	7.34	93.2	1.74:1
	C	7.57	96.2	1.44:1
	D	7.30	92.8	1.73:1
	E	7.01	89.0	1.87:1
Preform having final radius on one side, but smaller radius on other side. 	Overall	4.14	52.5	2.20:1
	A'	3.74	47.5	1.99:1
	B'	4.41	56.0	2.34:1
	C'	4.68	59.5	2.49:1
	D'	4.44	56.4	2.36:1
	E'	3.80	48.3	2.02:1
Final Form thereof. 	Overall	7.33	93.1	1.77:1
	A	7.27	92.4	1.93:1
	B	7.35	93.4	1.66:1
	C	7.44	94.5	1.52:1
	D	7.37	93.7	1.67:1
	E	7.29	92.6	1.94:1

^a This is the ratio of the relative density of the preformed compact to the apparent density of the powder; or, of the relative density of the final compact to that of the preformed compact.

compression ratio remains the same over the entire cross section. This is possible only if the powder-fill volume is proportionate to the compression ratio for each plane parallel to the pressure axis, and if lateral slippage of individual particles is prevented. The latter may be achieved by interrupting the molding at short intervals

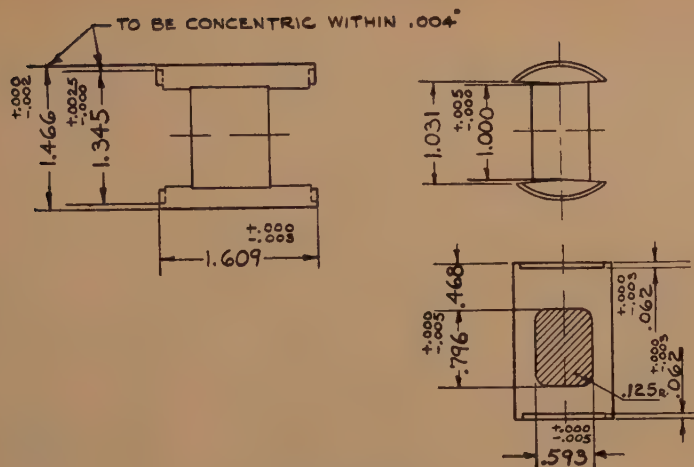
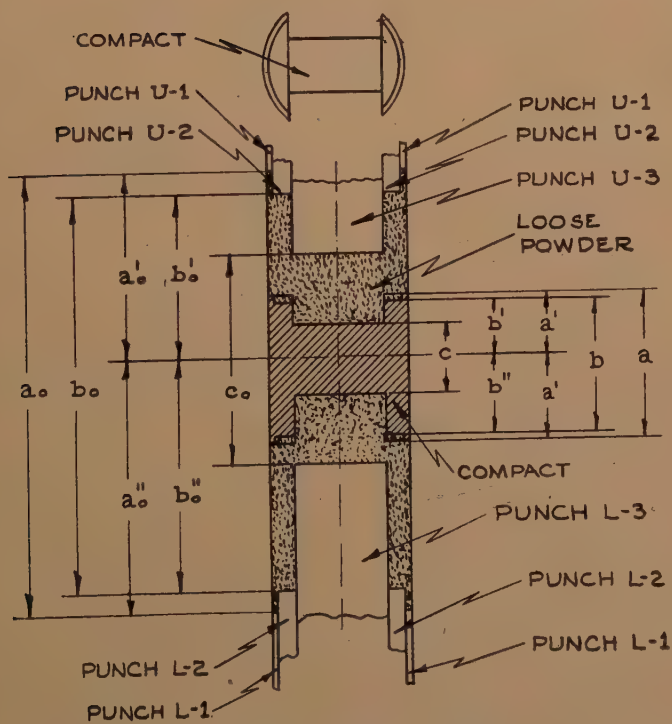


FIG. 9.—TYPICAL DESIGN OF ARMATURE.



COMPRESSION RATIO $a_o : a : b_o : b : c_o : c : 3 : 1$

FIG. 10.—IDEALIZED FILL AND MOLDING.

and metallizing the porous bodies, having shapes intermediate between the powder-fill shape and the final form of the dense body, by a heat-treatment. This may be

pressure method and can be carried out in a heavy hydraulic press as well as in a quick-acting mechanical one. A press of the latter type of 100 tons total capacity

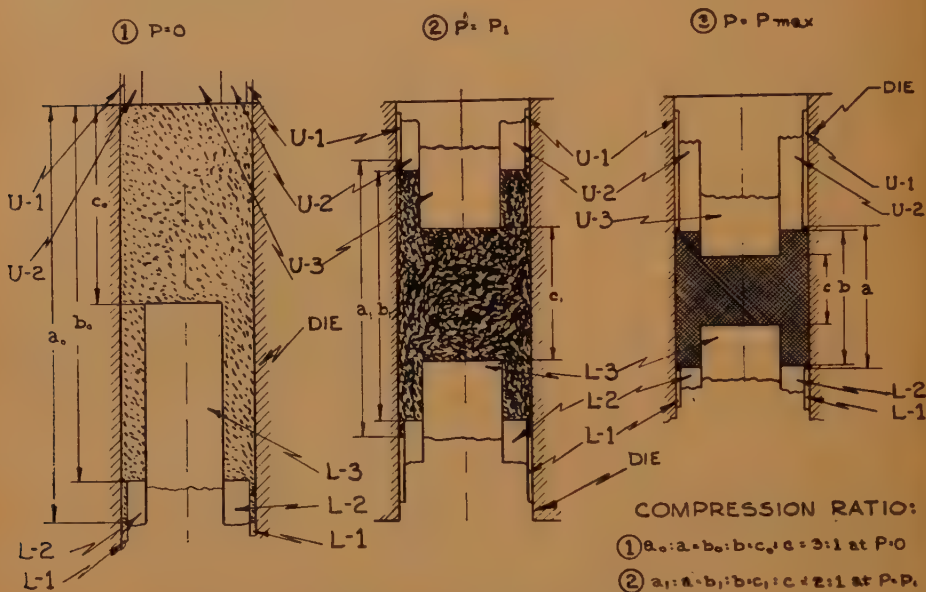


FIG. 11.—FLUSH LEVELING OF POWDER (THEORETICAL).

followed by subsequent stages of pressing and heating.

Another way, however, of maintaining the compression ratio and preventing lateral movements of the particles under pressure, which is considerably simpler and permits molding to final density in one press operation, has now been widely adopted and therefore calls for only brief description.

The powder is filled into a die cavity that forms the side walls of the compact in the usual manner. The top and bottom faces, however, are formed by punches, which consist of individual segments. These can move independently with adjustable speed and can also independently apply pressure of any desired magnitude up to the maximum press capacity. This type of molding may be called a differential

is now in operation, producing compacts at a rate of 10 pieces per minute in the manufacture of armatures (Fig. 8) for field-telephone generator sets. Fig. 9 is a drawing of one typical design. Fig. 10 illustrates an idealized fill and molding without leveling the powder flush with the die-top face, while Figs. 11 and 12 show the practical solution with flush leveling of the powder. Three stages with a compression ratio of 3:1 after filling, 2:1 at some intermediate stage of molding, and complete and uniform density at the maximum pressure, are indicated in Fig. 11. The three segments $U-1$, $U-2$, and $U-3$ of the upper punch, and the three segments $L-1$, $L-2$ and $L-3$ of the lower punch, have individual movement, velocity and pressure. The segments $U-3$ and $L-3$ are solid punches, while $U-1$, $U-2$, $L-1$ and

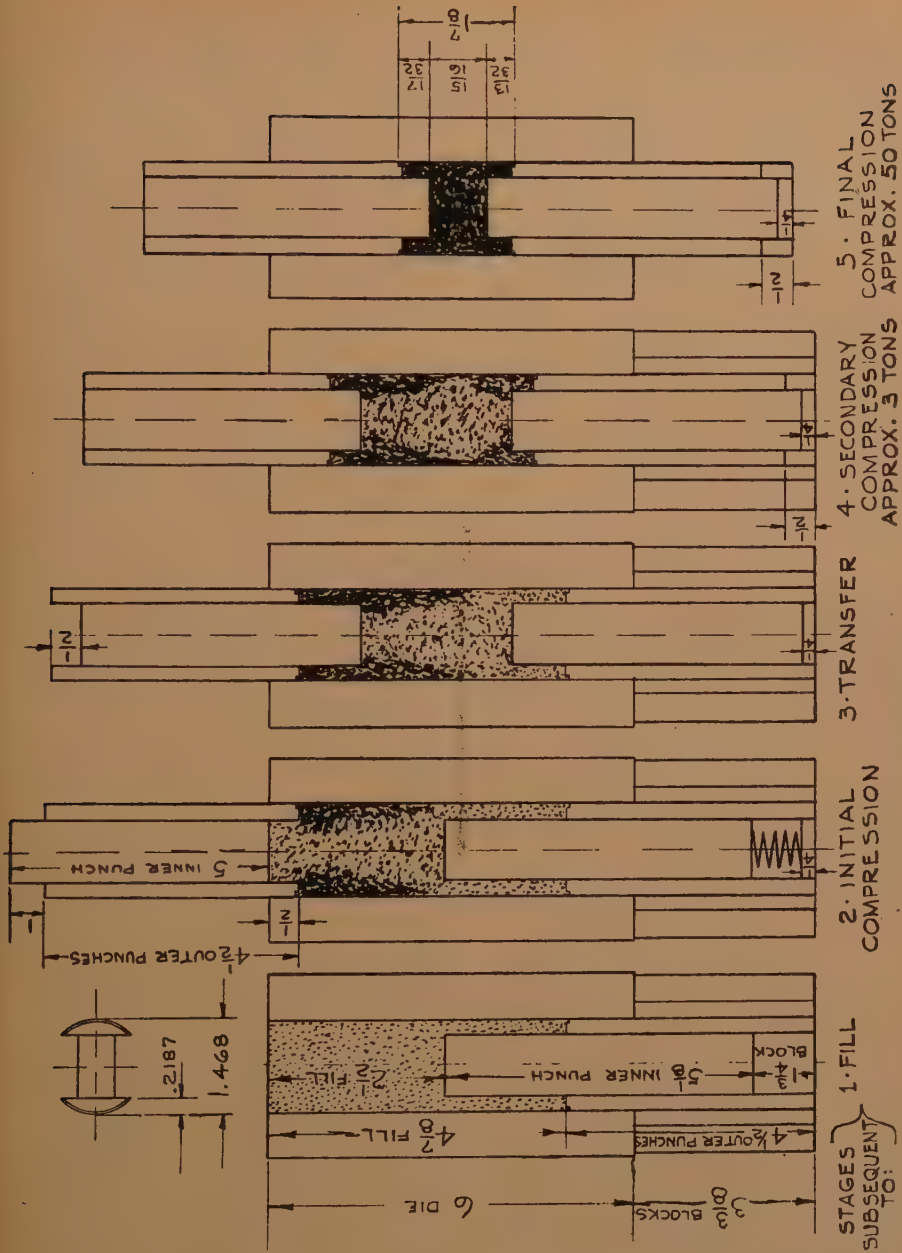


FIG. 12.—FLUSH LEVELING OF POWDER (ACTUAL).

L-2 are split punches of forklike shape. Fig. 12 gives the true stages between powder fill and final compression as carried out in the cam-driven mechanical press.

The advantages of this differential pressure method are evident: The individual action of each punch segment with regard to location, movement, velocity, and pressure permits a telescope type of double-action pressing procedure, which does justice to both demands so necessary for a high and uniform density; namely, the maintenance of a constant compression ratio over the cross section throughout the molding operation, and the elimination of lateral movement of particles caused by material concentration gradients of rather transitory character.

DISCUSSION

(*Frances H. Clark presiding*)

F. H. CLARK.*—Can Dr. Goetzel compare the magnetic properties such as permeability of the parts produced by powder metallurgy with pole pieces produced by conventional methods? How would the cost of the powdered metal part compare with a machined pole piece?

the pole pieces described in this paper are made. The material marked type 2 is about 85 to 90 per cent dense and contains other elements besides iron. The material marked type 3 is a pure electrolytic iron of about 96 per cent density. The magnetic properties of these materials are shown in Table 3, which gives also comparative data for Armco iron as far as available. The maximum permeability of materials 1 and 2 is 1500 at about 7000 lines per square centimeter, while it is about 3000 for materials 3, and 4500 for Armco iron. The maximum flux density in lines per square centimeter that was found practical with these materials was found to be 10,000 to 12,000 for material 1; 10,000 for material 2; and 14,000 for material 3; as compared with about 17,000 for Armco iron. The resistivity for material 2 is about five times that of Armco iron, while the other two materials are close to Armco iron.

With regard to the second question, the economics in powder metallurgy depend on many factors, such as the shape of the part, the quantity involved, what equipment can be made available without upsetting a balanced production, and, also, what kind of business can be built up with such magnetic parts. Hence, I could not venture a guess as to which method is more economical at this point.

TABLE 3.—*Properties of Soft Magnetic Materials*

Type	1 Reduced Iron, 90 Per Cent Dense	2 Iron Alloy, 85-90 Per Cent Dense	3 Electrolytic Iron, 96 Per Cent Dense	4 Armco Iron
Permeability (max.): $\mu = B/H \left(\frac{\text{Gauss}}{\text{Oersted}} \right)$	1,500	1,500	3,000	4,500
At B, lines per sq. cm.	7,000	7,000	7,000	7,000
Maximum usable flux density, B, lines per sq. cm.	10,000	10,000	14,000	17,000
Resistivity, percentage of Armco iron.	100	500	100	100

C. G. GOETZEL (author's reply).—I can answer the first question better than the second one. Three materials have been developed by us for soft magnetic applications. The material marked type 1 is about 90 per cent dense and produced from reduced iron powder. It is the same material from which

F. H. CLARK.—What was the shape of the test piece? Was it a ring or a rod?

C. G. GOETZEL.—The measurements were made on a flat ring of about $1\frac{1}{2}$ -in. diameter, $\frac{3}{8}$ in. wide, with square cross section. These rings were machined from flat plates.

F. V. LENEL.*—I have two questions. One

* Metallurgist, Western Union Telegraph Co., New York, N. Y.

* Moraine Products Division, General Motors, Dayton, Ohio.

is on the second piece. There are little lands on the piece and on some of the figures a special punch is shown for the lands. It seems to me that it should be possible to mold them without a special punch.

My second question concerns the first problem discussed; namely, the pole piece. Could you tell us something about the methods for presintering the preform, particularly with regard to sintering temperatures and times. I am interested because there seem to be two ways possible of attacking the problem. One way would be to get the ductility of the material during the presintering as high as possible, which would mean long sintering times and high sintering temperatures. The other way would be to get the material sintered as little as possible, which would mean short sintering times and low sintering temperatures and would, of course, result in a material of low ductility.

C. G. GOETZEL.—The special punches for the molding of the small lands in the armature are shown only in the diagrammatic sketches of Figs. 10 and 11, in order to clarify the molding principle. In practice it was found unnecessary to use these very thin punch segments, and the lands could be molded and coined perfectly with the simpler punches shown in Fig. 12, since the difference in height is very little. Incidentally, the outer punch segments are combined in forklike fashion and are linked to one cam of the press.

As for the second question, in making the particular pole-piece shape here discussed it was possible to form only one intermediate shape, provided the proper powder and correct sintering conditions were employed. The compact was presintered first at about 800°C. for about 15 min. in a controlled atmosphere of dissociated ammonia. In this treatment, the volatilized decomposition products of the lubricant, initially added to facilitate molding, were driven off. At the same time, the preform, which had only approximately 50 per cent density after molding at 5 to 15 tons per sq. in., was sufficiently strengthened to permit transfer to a high-temperature continuous furnace, in which the part was reheated to a temperature of 1100°C. Sintering at this temperature for 15 min. in dissociated ammonia was found sufficient for the degree of ductility

needed in the part to withstand the severe plastic deformation in the coining operation.

The idea behind the short sinter was to just enable the formation of sufficient sinter bonds between the individual loosely agglomerated particles, so that the compact could then be further deformed in the next pressing operation. From Fig. 7, it is evident that a severe deformation takes place in the final pressing operation, and this sometimes caused severe fissures because first the upper plunger with the correct radius began molding, thereby condensing the two side lengths, then the lower, flat plunger, would start pressing on these two projections, while the middle remained unsupported. The radius section became supported only toward the end of the pressing operation, where fairly high pressures were reached. Certain powders did not permit sufficient sinter bonds to form during heat-treating, with the result that the body could not withstand the uneven stress application, and fractures occurred, especially in the critical center section. However, with the right kind of powder, such as a reduced brand having not too spongy particles, the required severe deformation during repressing could be carried out without these failures.

MEMBER.—What pressures were used on that 6 per cent?

C. G. GOETZEL.—The pressure is somewhat connected with the question of the powder used. If the powder is of a high apparent density, a high relative density of the compact can possibly be obtained with somewhat lower pressures than if a very fluffy and light-weight powder is used. The 96 per cent dense material can be obtained with a heavy electrolytic iron powder of, say, 3.0 grams per cubic centimeter apparent density, by first pressing at 50 tons per sq. in. and, after sintering, repressing again, at 50 tons per sq. in., followed by resintering. If an electrolytic iron of 2.7 grams per cubic centimeter density is used, it is necessary to coin twice at 50 tons per sq. in.; in other words, to go through three pressing operations. It generally does not pay to go much above 50 tons per sq. in., because the dies do not stand up well under these very high pressures unless the parts are fairly isometric and do not cause any severe local stresses on certain projections.

Hot-pressing of Iron Powders

By OTTO H. HENRY,* MEMBER A.I.M.E. AND J. J. CORDIANO†

(Chicago Meeting, February 1946)

THOUGH powder metallurgy is one of the oldest of metallurgical processes, it is in its infancy as a branch of the modern field of metallurgy. As early as 3000 B.C., the ancients produced implements and weapons of iron by reducing iron ore in a charcoal fire and forging the resultant sponge while still hot into the desired shape. Melting and casting soon superseded the powder metallurgy practice, and it was not until the turn of the twentieth century that powder metallurgy was applied to the commercial manufacture of tungsten lamp filaments.

From this beginning, the use of the powder metallurgy process spread to the manufacture of porous oil-impregnated bearings, cemented carbide tools, contact points, diamond grinding wheels, clutch facings, starter brushes, resin-bonded radio cores, magnets, metallic filters, and other parts. More recently, and particularly during the present war, there has been a definite trend toward the manufacture of machine parts by this process in competition with the more conventional fabricating methods.

Notwithstanding these many developments, scientific progress has been slow. While many articles on powder metallurgy have appeared in the press and various

publications, there have been too few contributions to our technical societies, with the result that there is a dearth of the type of information necessary for the full development of this science. It is of primary importance that the results of research and development be freely disseminated if powder metallurgy is to realize its fullest potentialities.

PURPOSE OF INVESTIGATION

Excluding the refractory metal field, all commercial powder metallurgical products made by a cold compressing and sintering operation contain voids. These voids can be substantially eliminated by subsequent severe working and heat-treatment, but such practice has not proved economical in most applications.

By applying heat during the compressing operation, plastic deformation of the powder particles is substantially increased, and the resultant compact or briquette is practically free of voids. However, hot-pressing has many attendant problems, which at present preclude its use in the manufacture of precision parts. The more important of these are to devise:

1. A die steel capable of withstanding high pressures at elevated temperatures.
2. A high-temperature lubricant capable of preventing excessive die wear and welding of the compact to the die walls.
3. A method of retaining a neutral or reducing atmosphere in the compacting zone of the die assembly.
4. A means of ejecting the hot-pressed specimen into a neutral atmosphere until reasonably cold.

Based on thesis submitted in partial fulfillment for M.M.E. degree at the Polytechnic Institute of Brooklyn in June 1941 by J. J. Cordiano. Manuscript received at the office of the Institute Jan. 8, 1945; revised May 5, 1945.

Listed for New York Meeting, February 1945, which was canceled. Issued as T.P. 1919 in METALS TECHNOLOGY, October 1945.

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† Research Engineer, Hardy Metallurgical Co., New York, N. Y.

5. A means of confining to the die cavity the heat developed.

6. A design of a soundly engineered machine for mass production.

APPARATUS

Three methods are generally used for supplying heat to the specimens being hot-pressed: (1) induction; (2) passing a

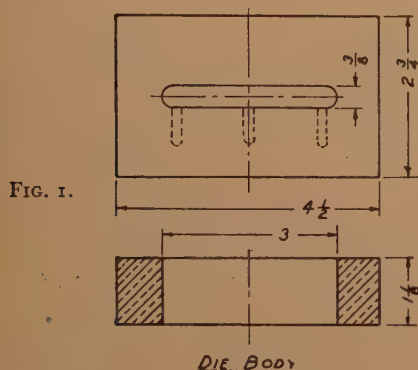


FIG. 1.

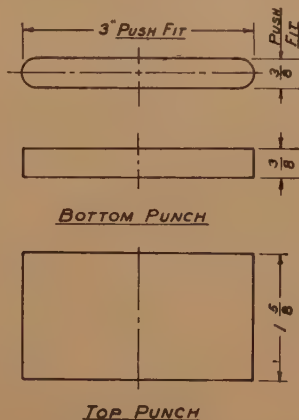


FIG. 2.

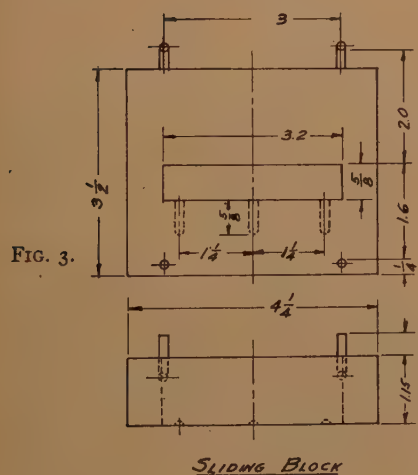


FIG. 3.

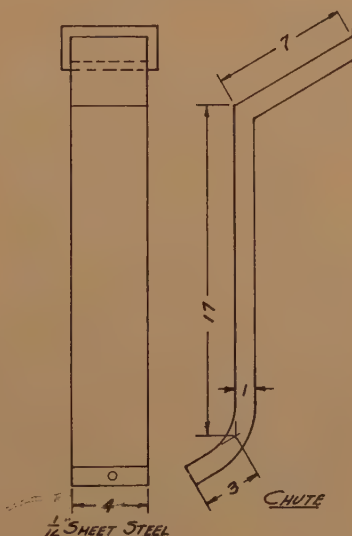


FIG. 4.

FIG. 1.—DIE BODY.
FIG. 2.—PUNCHES.
FIG. 3.—SLIDING BLOCK.
FIG. 4.—CHUTE.

All these requirements must be met or by-passed before hot-pressing can become a successful commercial procedure. This investigation is concerned with determining the properties of hot-pressed specimens of electrolytic iron powder.

current through the highly resistant powder mass; (3) enclosing the entire die assembly in a furnace. (Because of its relative simplicity, the latter method was used in this investigation.)

The details of the apparatus are shown

in Figs. 1 through 10. The die, upper ram, and lower punch, and sliding block were made of heat-resistant steel. The die block was made of cast iron and the chute of

1. To facilitate handling during hot-pressing, the iron powder was precompacted cold at 20 tons per sq. in. into 3 by $\frac{3}{8}$ by $\frac{5}{8}$ -in. specimens. The die lubricant

FIG. 5.

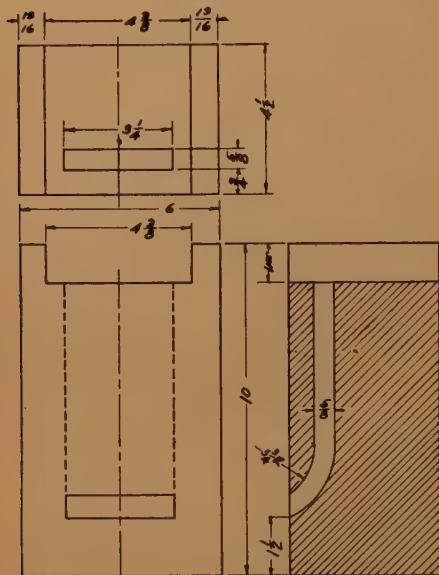


FIG. 6.

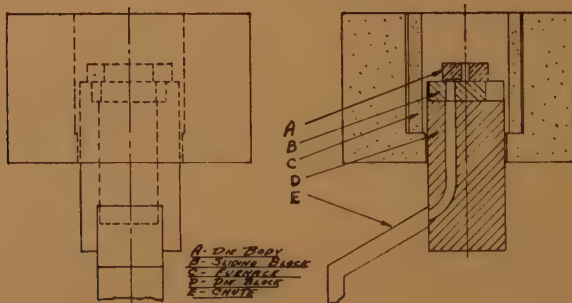
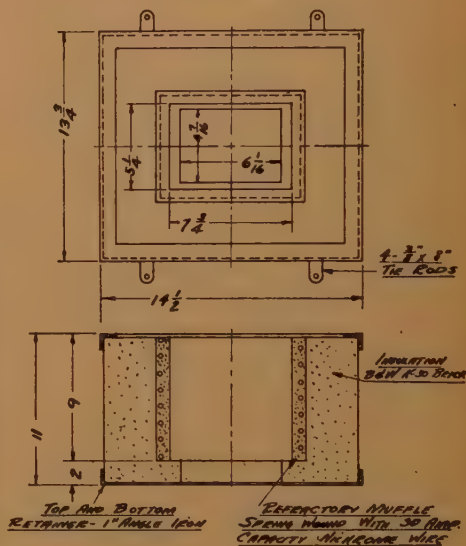


FIG. 7.

FIG. 5.—DIE BLOCK.

FIG. 6.—ELECTRIC RESISTANCE FURNACE.

FIG. 7.—DIE ASSEMBLY.

sheet steel. The chemical analysis and elevated-temperature properties of this steel are shown in Table 1.

MATERIAL AND PROCEDURE

The metal powder used in these tests was an electrolytic iron having the characteristics listed in Table 2.

was composed of one gram of stearic acid dissolved in 20 cc. of carbon tetrachloride.

2. The hot-pressing punches and die parts were rubbed with flake graphite to provide high-temperature lubrication.

3. With the die assembly as indicated in Fig. 7, the system was purged with dry nitrogen before the furnace was brought to

FIG. 8.

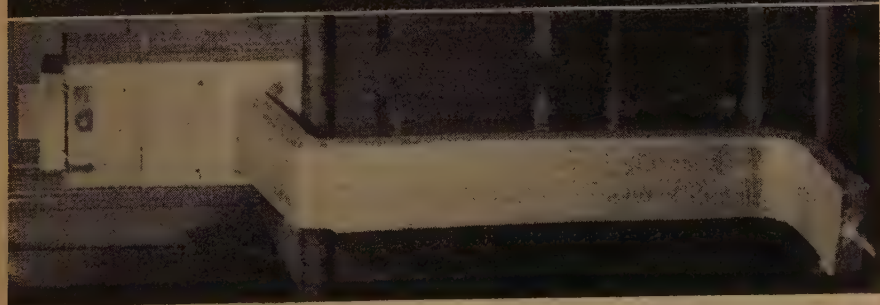


FIG. 9



FIG. 10.



FIG. 8.—PUNCH, DIE BODY, SLIDING BLOCK, CAST-IRON DIE BLOCK AND CHUTE.
FIG. 9.—FURNACE IN PLACE OVER PARTIAL ASSEMBLY SHOWN IN FIG. 8.
FIG. 10.—HOT-PRESSING ASSEMBLY IN PLACE ON 75-TON HYDRAULIC PRESS.

TABLE I.—*Analysis and Properties of Punch and Die Steel Used in Apparatus*

Chemical Analysis, Per Cent			
C.....	0.33	Ni.....	19.70
Mn.....	0.49	Cr.....	8.31
Si.....	1.16	Fe.....	Bal.

Properties at Elevated Temperatures

Temperature, Deg. C.	Tensile Strength, Lb. per Sq. In.	Proportional Limit, Lb. per Sq. In.	Elongation, Per Cent in 2 In.
20	112,500	45,200	
205	102,000	45,600	21.0
480	90,800	40,100	20.0
595	80,000	35,500	19.7
650	74,000	35,800	19.3
705	65,400	26,200	18.5

and through the die cavity. Grooves cut into the bottom of the die permitted the flow of gas from the sliding block into the die cavity. The nitrogen served two purposes: to prevent oxidation of the die parts and to provide a means for purging the hot die cavity with hydrogen without forming an explosive mixture.

4. When the furnace had reached temperature, hydrogen was passed through the system instead of nitrogen. Before it was led into the chute, the hydrogen was purified by bubbling through sulphuric acid traps and passing through phosphorus pentoxide drying towers. The hydrogen escaping from the upper portion of the die assembly was ignited and allowed to burn.

temperature. Gas flowed through the system by passing up through the chute *E* and die block *D* into the sliding block *B*

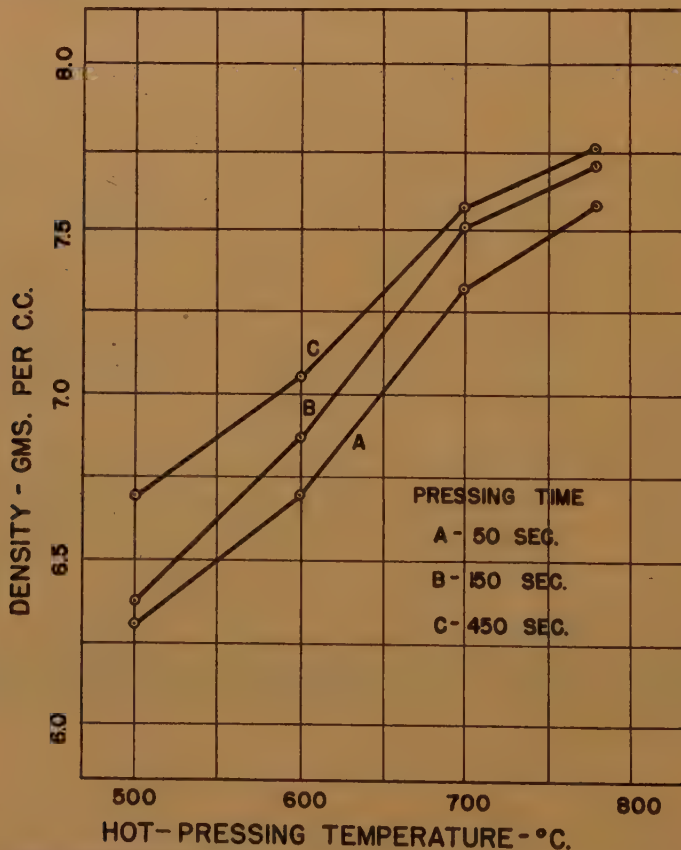


FIG. 11.—RELATION BETWEEN DENSITY AND PRESSING TEMPERATURE FOR INDICATED TIME.

TABLE 2.—*Characteristics of Electrolytic Iron Powder Investigated*

Apparent density in hall flowmeter, grams per c.c.....	2.4
Flow (for 50 grams) in hall flowmeter, sec....	46
Hydrogen loss at 850°C. for one hour at temperature in dry hydrogen, per cent.....	0.3

Chemical Analysis, Per Cent	Screen Analysis, Per Cent
C..... 0.005	+100..... 1.0
Mn..... 0.002	—100+150..... 10.5
Si..... 0.002	—150+200..... 21.5
P..... 0.001	—200+250..... 11.0
S..... 0.004	—250+325..... 13.0
Ni..... 0.008	—325..... 43.0

5. The loosely pressed compact was placed in the heated die and left for 10 min. to soak.

6. A pressure of 10 tons per sq. in. was applied for the predetermined time interval (50, 150 or 450 sec.).

7. The specimen was ejected by releasing the pressure, positioning the sliding block so that its cavity coincided with the die cavity above, ejecting the compact into the sliding-block cavity, and then positioning the sliding block so that its cavity coincided with the die-block cavity below. In this position the compact fell through the die block and into the chute.

8. When the specimen had cooled, the hydrogen was replaced by nitrogen, the specimen removed, and the system completely purged with nitrogen before hydrogen was again used.

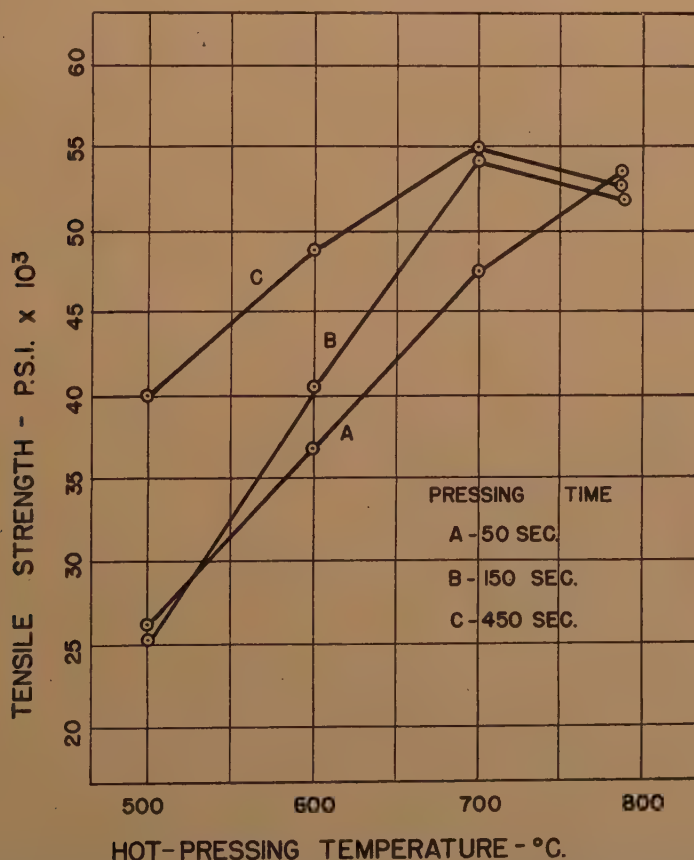


FIG. 12.—RELATION BETWEEN TENSILE STRENGTH AND PRESSING TEMPERATURE FOR INDICATED TIME.

TABLE 3.—Results

Temperature, Deg. C.	Time, Sec.	Density, Grams per c.c.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 1 In.	Brinell Hard- ness, 500-kg. Load, 10-mm. Ball
500	50	6.31	26,200	0	50
500	150	6.38	25,500	0	51
500	450	6.71	39,800	1.0	63
600	50	6.70	36,900	0.5	62
600	150	6.89	40,800	1.0	77
600	450	7.05	48,800	2.0	80
700	50	7.32	47,800	1.0	90
700	150	7.52	57,300	12.0	95
700	450	7.58	57,500	27.0	100
780	50	7.59	54,100	22.0	101
780	150	7.71	52,400	32.0	93
780	450	7.76	52,900	37.0	96

9. The die was quenched in oil, rubbed with graphite again, and replaced in the assembly for the next run.

10. The compacts obtained by hot-pressing were machined to conform to standard A.S.T.M. specifications for tensile specimens of $\frac{1}{4}$ -in. diameter.

11. Tension, density and hardness tests were conducted on the specimens. The tensile tests were conducted on a 10,000-lb. Riehle universal testing machine. The density determinations were made by the water-immersion method. To guard against absorption of water, the specimens were coated before immersion with a wax of known specific gravity. Hardness tests were conducted on a Brinell hardness tester using a 500-kg. load and a 10-mm. ball.

12. A microscopic examination was made of each specimen (Figs. 15 and 16).

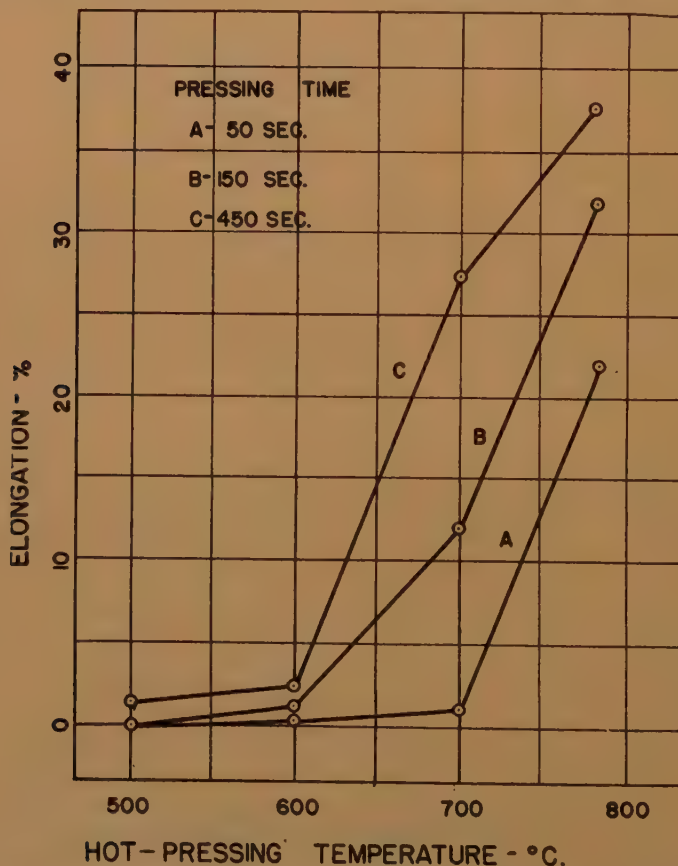


FIG. 13.—RELATION BETWEEN DUCTILITY AND PRESSING TEMPERATURE FOR INDICATED TIME.

DISCUSSION OF RESULTS

The results of these tests (Table 3) indicate the potent influence of time and temperature on the physical and mechani-

temperature and to a lesser extent with increasing time at temperature. If intermediate points were obtained, the temperature curves would probably take the

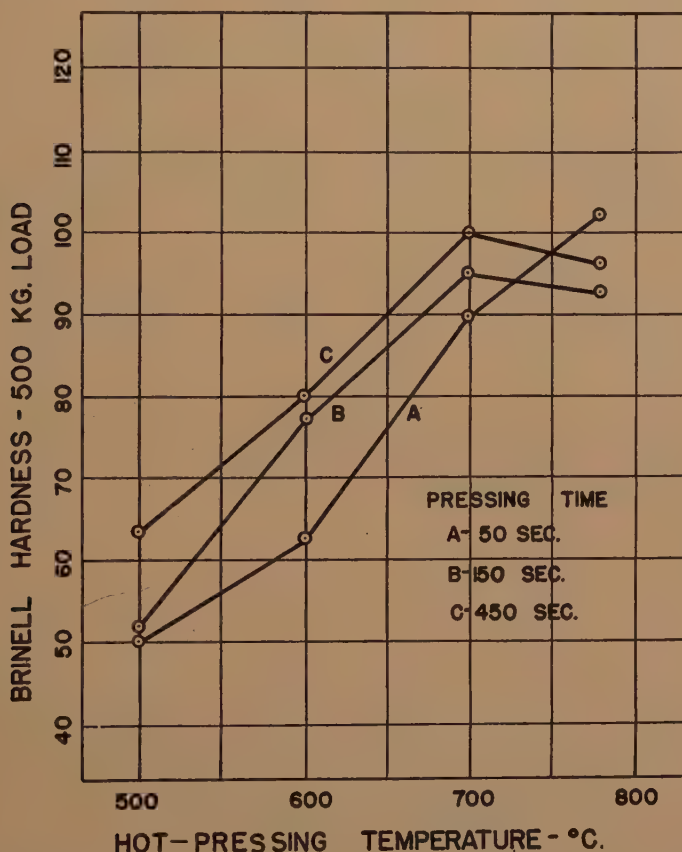


FIG. 14.—RELATION BETWEEN HARDNESS AND PRESSING TEMPERATURE FOR INDICATED TIME.

cal properties of hot-pressed iron powders. These properties are dependent upon the amount and rate of diffusion, which in turn depends on the number and area of intraparticle contacts, as well as on the amount of plastic deformation to which the compact is subjected. Increasing temperature and time at temperature under sustained pressure tends to increase each of these effects *individually*, with cumulative results.

Density.—The curves in Fig. 11 show a decided increase in density with increasing

form of S-curves with the maximum slope between 600° and 700°C. Within this range the effects of increased plastic deformation of the density are marked. Above 700°C., the density increases at a slower rate and for a 450-sec. sustained pressure period at 780°C. is 99.1 per cent of the theoretical density of solid iron.

Hardness.—The Brinell hardness curves (Fig. 14) are influenced by several factors. With increasing density, higher readings are obtained, even though there may be no actual increase in the hardness of the metal,



FIG. 15.—COMPACT HOT-PRESSED AT 500°C. FOR 50 SECONDS AT 10 TONS PER SQUARE INCH.
ORIGINAL MAGNIFICATION 500.
Etched with 1 per cent Nital. Structure shows extreme distortion of particles with little if any signs of recrystallization.



FIG. 16.—COMPACT HOT-PRESSED AT 780°C. FOR 450 SECONDS AT 10 TONS PER SQUARE INCH.
ORIGINAL MAGNIFICATION 1000.
Structure shows absence of particle boundaries and a completely recrystallized structure.

because there is more metal available to resist the indentation of the ball. Since the specimens are maintained at

strong bonding resulting from hot-working and the complete recrystallization of the grain structure.

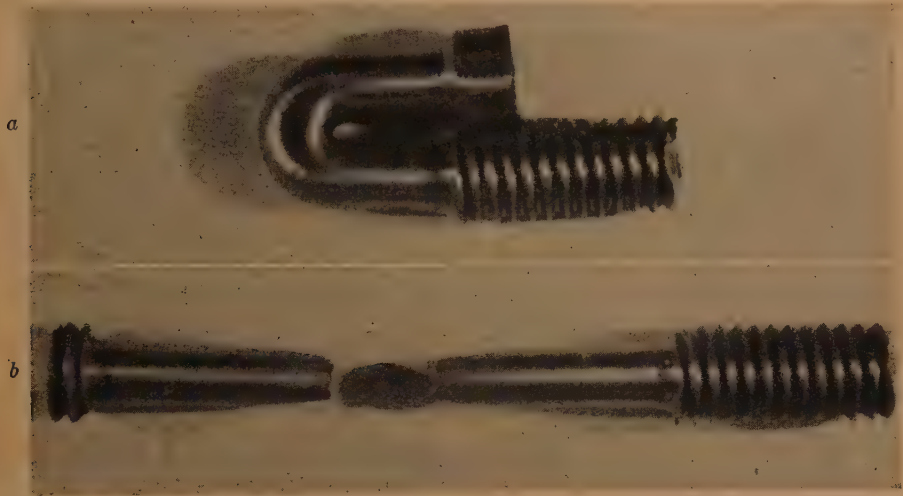


FIG. 17.—IRON-POWDER COMPACTS HOT-PRESSED AT 700°C . FOR 450 SECONDS AT 10 TONS PER SQUARE INCH.

a. 180° bend test.

b. tensile test, 57,500 lb. per sq. in.; 27 per cent elongation.

temperature for only a short time, however, the cold-working that results from plastic deformation must account for some of the increase in hardness readings. Support for this contention is indicated in the results for specimens hot-pressed above 700°C . The metal is hot-worked and the annealing effects are indicated on the curves by the decrease in hardness.

Tensile Strength and Elongation.—The curves for tensile strength (Fig. 12) and elongation (Fig. 13) clearly show the advantages that may be gained from hot-pressing. The increase in tensile strength up to 700°C . is caused by increasing intraparticle bonding. The increase in contacting particle surfaces and diffusion rates with increasing temperatures under sustained pressure are mainly responsible for this bonding.

The elongation values, though nominal at the lower temperatures, increase rapidly at the higher temperatures because of the

CONCLUSIONS

The properties that can be obtained on hot-pressed iron powders are far superior to the properties of cold-pressed and sintered iron powders. However, the time, temperature, and pressure requirements are too severe for present-day commercial equipment. With advances in processing and materials, the hot-pressing of metal powders should take its place as an important method of fabricating metal.

DISCUSSION

(R. P. Seelig presiding)

L. H. DEWALD.*—I would be interested in knowing what effect on the physical properties Mr. Cordiano has found by varying the rapidity at which he arrives at his critical pressing temperature.

J. J. CORDIANO (author's reply).—We did not conduct any tests on varying the rapidity

* Massachusetts Institute of Technology, Cambridge, Massachusetts.

at which we attained our critical pressing temperatures to determine the effect on the physical properties. Such tests were not included in the scope of this investigation. We did not feel that variations in heat-up time would make significant differences in the physical properties of the hot-pressed specimens.

L. H. DEWALD.—The reason I asked the question is that there are several humps in the curves due to recrystallizing and annealing, and I thought if you had brought the temperature up very rapidly and pressed, you might have gotten stronger and harder compacts.

J. J. CORDIANO.—In what way? The effects of cold-working would still remain.

L. H. DEWALD.—There would be little or no annealing effect due to the heat; sintering would occur almost instantaneously with little structural change.

J. J. CORDIANO.—You must consider that the pressing temperatures were within the range of 500° to 800°C. and the over-all times at temperature were short. It is my belief that there could hardly be much difference in the hardness or the amount of annealing of the finished specimens by varying time for initial heat-up periods. Considerable plastic deformation occurs during hot-pressing and, considering the operating temperatures, we feel that cold-working took place during hot-pressing for all except the tests at the highest temperature.

L. H. DEWALD.—In hot-pressing cemented carbides these variations are found, and I wondered whether you found similar effects in your investigation.

JOHN WULFF.*—The steel used by Mr. Cordiano for hot-pressing loses hardness rapidly at 500°C. and above. We have found stellite dies to be superior for hot-pressing between 500° and 800°C. These are somewhat superior from an oxidation standpoint to the high

cobalt-tungsten-iron age-hardenable alloys recommended by Sykes a number of years ago. There is some present indication that cast alloys containing a higher percentage of chromium than the stellites may even be superior in the region 800° to 1000°C. Originally recommended for heat and creep-resistant application, some of the high-melting-point alloys similar to those suggested by Hamilton-Adams,* and containing over 50 per cent chromium, with a high percentage of molybdenum or tungsten (c. 20 to 25 per cent) and some residual iron (10 to 20 per cent) have proved useful for hot-pressing dies.

R. P. SEELIG.†—This question of die materials is indeed very interesting. We have considered going up to higher temperatures and higher pressures. In some cases, the approach is the other way around, using high temperatures at low pressures, nonmetallic die materials can be used. Would anyone care to comment on that phase of hot-pressing?

C. G. GOETZEL.‡—Some years ago, we studied this question of die materials and, in agreement with Professor Wulff's statement, we found that metallic die materials could be used up to and including 800°C. High-speed steel alloys containing 18 per cent tungsten were found most suitable and did not lead to difficulties in welding of the hot-pressed compact to the die.

When using these metallic dies at 800°C. we were still able to apply pressures up to 20 tons per sq. in. and thus obtain complete consolidation of the compact. On the other hand, when we raised the temperature to only 900°C., the die material became suddenly very soft and the welding difficulties became much greater. We therefore looked for a non-metallic die material for work above 800°C. It was decided to use graphite because of its good performance in hot-pressing of cemented carbides, although the direct contact between the iron compact and the graphite die walls resulted in strong surface carburization above

* *Iron and Steel* (1943-44) 17, 284.

† Powder Metallurgy Inc., Long Island City N. Y.; now Electro Metals Corporation, Yonkers, New York.

‡ Electro Metals Corporation, Yonkers, New York.

* Professor of Metallurgy, Massachusetts Institute of Technology, Cambridge Massachusetts.

1000°C., even if the contact was only for a short time. We hoped to obtain complete consolidation of the iron compact before the melting temperature of cast iron was reached; e.g., 1140°C. Unfortunately, we failed in this attempt. Even the softest iron powder we could secure at that time made too rigid a compact at temperatures up to 1140°C. to be compressed into a completely dense body at those very low specific pressures permissible with the graphite die; e.g., 2 tons per sq. in. max. Not only was the consolidation inhibited by the fact that in plain iron no liquid phase exists that would increase plasticity and shrinkage, as with cemented carbides, but the carburized surface caused additional resistance to plastic deformation of the compact. Thus the average density did not exceed about 90 to 92 per cent.

Another peculiar phenomenon was that in surpassing the transformation of alpha to gamma iron some 10°, a marked stiffening of the compact and a greater resistance to deformation under the operating pressure was suddenly observed. For a given pressure, for example, 2 tons per sq. in., a higher density was obtained when pressing at 880°C. than when pressing at 920°C. This increased rigidity was lost only at considerably higher temperatures—actually, only at temperatures in the order of 1100° or 1200°C. the same plasticity, and, therefore, density was obtained that could already be observed at a temperature just below the transformation temperature.

J. J. CORDIANO.—These experiments were conducted as part of a master's thesis and our main interest was in the physical properties of hot-pressed iron powders rather than obtaining data on die steels. We feel our choice of die steel was suitable for our experimental work in that the pressures applied were below the yield strength of the die material at the highest pressing temperature. We realize, of course, that a number of other types of steels or metal alloys may be more suitable for the purpose, but we point to the fact that the results given in this paper are the first published information in this country, to our knowledge, on the mechanical properties of hot-pressed iron-powder specimens large enough to permit machining of tensile bars.

W. N. PRATT.*—The paper by Henry and Cordiano has once again pointed out the necessity for hot-press experimental work and has definitely shown the need for such equipment. However, a few things should be added to it; for instance:

A neutral atmosphere is not always necessary. Additions can be made to the green compact or to the powder before loading into the die that will remove oxides at the sintering temperature and tend to maintain an atmosphere that is not necessarily neutral in the die.

I believe that a study should be made of temperature vs. compactability on the same specimen. This is easily done by measuring the amount of travel of the punch at varying temperatures during the same hot-pressing cycle. The figures achieved by this study are extremely important in forecasting the actual ability of a powder to be used in commercial hot-pressing. Usually it is easy to find the temperature at which the compact or the powder shows a very definite increase in plasticity. It is useless to use more than a light pre-load until this temperature has been reached. The pre-load should consist of just a few hundred pounds per square inch, used merely to keep the die in the closed condition and to follow the powder as it shrinks in the heating. When the temperature of plasticity has been reached, a final pressure should be applied rapidly in order to overcome friction on the die walls.

One other fact should be brought forward at this point: High-temperature lubricants are available that prevent welding of the compact to the die wall. These usually consist of ground mica. The contamination of the surface by mica is not bad because no electrolytic couple is set up.

J. J. CORDIANO.—It is our contention that it is necessary to maintain the neutral or deoxidizing conditions not only during the pressing operation but also during the cooling cycle. Metal-powder parts made to close tolerances are not of much value if they have pitted and oxidized surfaces.

Mr. Pratt mentions that only a light pre-load is necessary until the temperature has been reached and then a final quick pressure application to obtain a hot-pressed part.

* American Electro Metal Corporation, Yonkers, New York.

Our investigation was aimed at determining the effects of time at pressure and temperature on the physical properties of hot-pressed specimens. Our results show that variations in time at pressure and temperature show significant changes in the physical properties of the hot-pressed parts.

We do not believe that ground mica as a lubricating medium will prove commercially practical. In a continuous hot-pressing operation, we believe there will be a buildup of mica in the die cavity, or the hot-pressed specimens will have mica flakes embedded in their surfaces.

Notes on Copper-base Compacts and Certain Compositions Susceptible to Precipitation-hardening

By F. R. HENSEL,* MEMBER A.I.M.E., E. I. LARSEN† AND E. F. SWAZY†

(Chicago Meeting, February 1946)

HIGH strength, high-conductivity copper-base alloys have found considerable use in the resistance welding and electrical industry in the form of castings, forgings, or wrought products. There are a number of parts utilized by these industries which would lend themselves to manufacture by powder metallurgical methods provided the required physical and electrical properties are obtainable with such methods. The present paper describes the results of a study of certain copper-base powder metallurgical products susceptible to precipitation hardening.

COPPER POWDERS

The general types of commercially available copper powders are flake, spherical and electrolytic. Micrographs of these three types are shown in Figs. 1, 2 and 3. The difference in particle shape is pronounced and obvious. The type of powder used is determined, or at least indicated, by the final properties desired in the finished article. The type of powder employed during the present investigation was electrolytic powder shown in Fig. 3, and was chosen because of its particular adaptability to the work described in this paper. The screen and chemical analyses of this powder are shown in Table I.

In the preparation of compacts of high electrical conductivity, the purity of the

copper powder is of importance in addition to other factors, such as density and the state of internal stresses. These variables were studied briefly by pressing a number of compacts to various pressed densities, sintering them for one hour in hydrogen at 975°C. and repressing. The size of the finished compacts was $\frac{1}{4}$ by $\frac{3}{4}$ by 8 in. The time interval from the application to the termination of pressure was approximately 20 sec. Some of the compacts were annealed before testing. The results are listed in Figs. 4 to 8, inclusive.

TABLE I.—Typical Screen and Chemical Analyses of Electrolytic-copper Powder

APPARENT DENSITY = 2.5 GRAMS PER C.C.		CHEMICAL ANALYSIS, PER CENT	
Mesh Size	Per Cent Retained		
100.....	0.0-0.2	Iron.....	0.25
150.....	1.0-3.5	Zinc.....	0.10
200.....	5.0-9.0	Oxygen.....	0.25
250.....	1.5-3.5	Copper.....	Balance
325.....	15.0-20.0		
-325.....	65.0-75.0		

In Fig. 4 the curves of pressed density vs. compacting pressure, and sintered density versus compacting pressure show the typical direct relationship of pressure and density. Compacting pressures exceeding about 30 tons per sq. in. result frequently in expansion during sintering for the type of powder used.

Fig. 5 indicates that variations in the initial pressed density within the range of about 5 to 6 grams per c. c., affect only slightly the pressure required to obtain a

Manuscript received in the office of the Institute Nov. 20, 1944. Listed for New York Meeting, 1945, which was canceled. Issued as T.P. 1810 in METALS TECHNOLOGY, August 1945.

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† Metallurgical Department, P. R. Mallory and Company, Incorporated.



FIG. 1.—FLAKE COPPER POWDER. $\times 200$.

FIG. 2.—SPHERICAL COPPER POWDER. $\times 200$.

FIG. 3.—ELECTROLYTIC COPPER POWDER. $\times 200$.

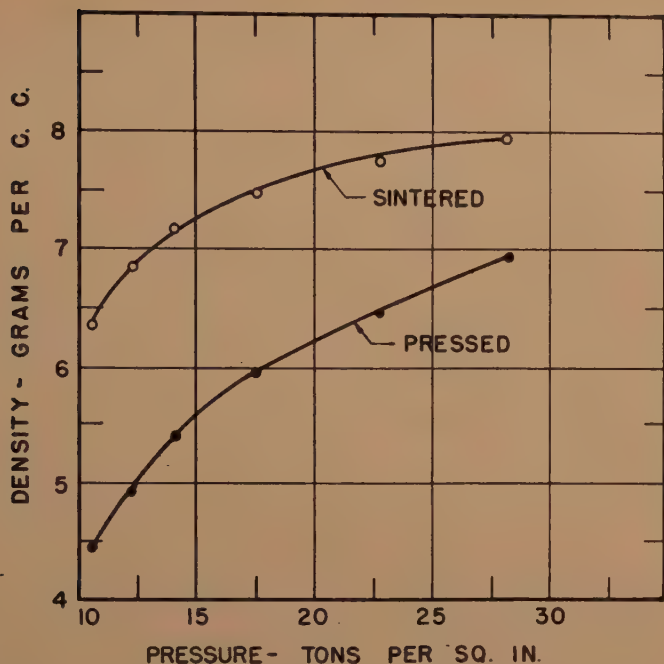


FIG. 4.—DENSITY OF ELECTROLYTIC COPPER-POWDER COMPACTS AS PRESSED AND SINTERED FOR ONE HOUR IN HYDROGEN AT 975°C.

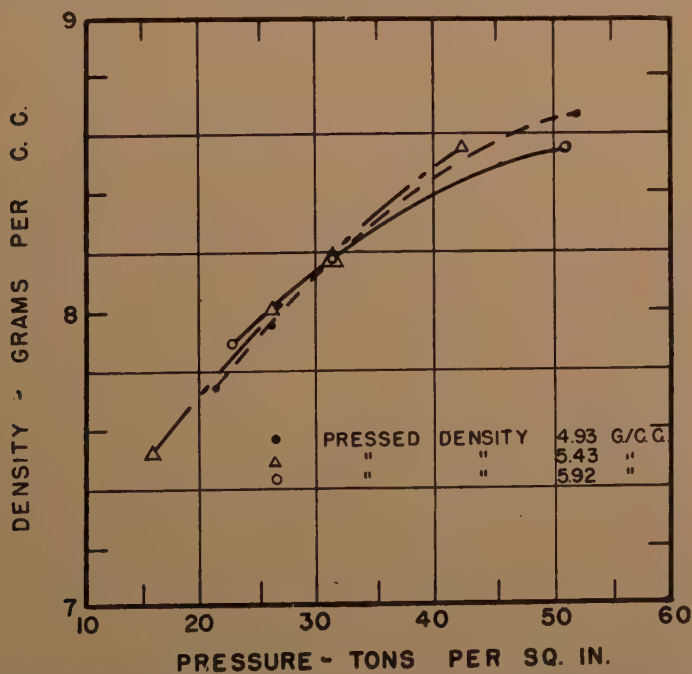


FIG. 5.—DENSITY OF ELECTROLYTIC COPPER-POWDER COMPACTS PRESSED TO VARIOUS DENSITIES SINTERED ONE HOUR IN HYDROGEN AT 975°C. AND RE-PRESSED AT VARIOUS PRESSURES.

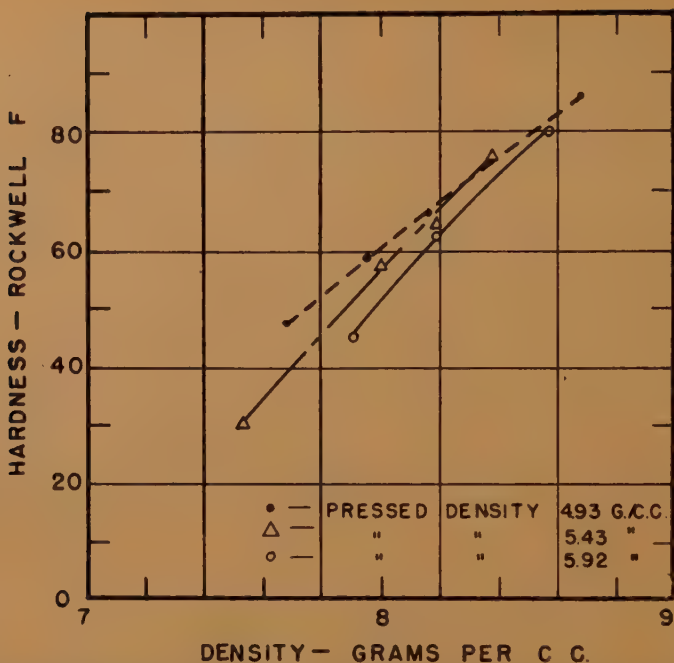


FIG. 6.—HARDNESS AS A FUNCTION OF THE REPPRESSED DENSITY OF ELECTROLYTIC COPPER-POWDER COMPACTS PRESSED TO VARIOUS DENSITIES, SINTERED ONE HOUR IN HYDROGEN AT 975°C. AND REPPRESSED.

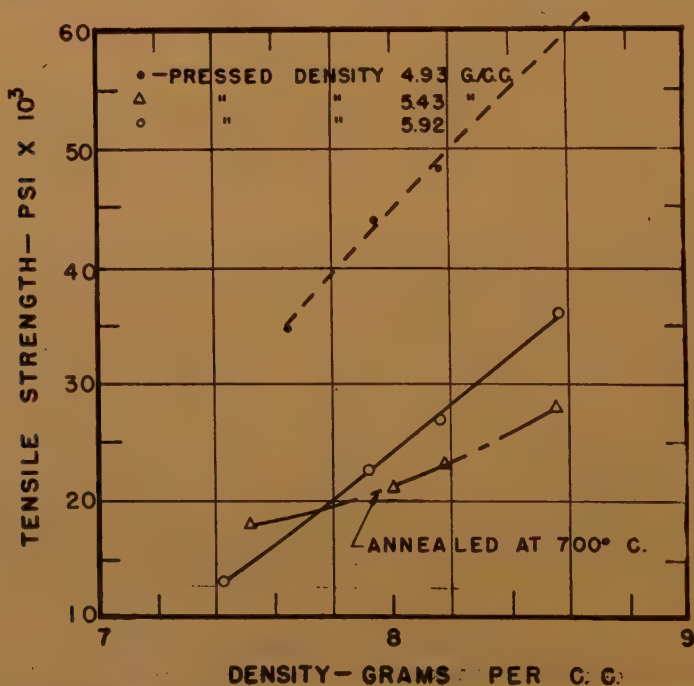


FIG. 7.—TENSILE STRENGTH AS A FUNCTION OF THE REPPRESSED DENSITY OF ELECTROLYTIC COPPER-POWDER COMPACT PRESSED TO VARIOUS DENSITIES, SINTERED ONE HOUR IN HYDROGEN AT 975°C. AND REPPRESSED.

given repressed density after sintering. The range of 5 to 6 grams per c.c. pressed density is convenient for commercial powder metallurgical applications.

In Fig. 8 the electrical conductivity is shown as a function of the final density. As might be expected, the material having the lowest initial (pressed) density has the

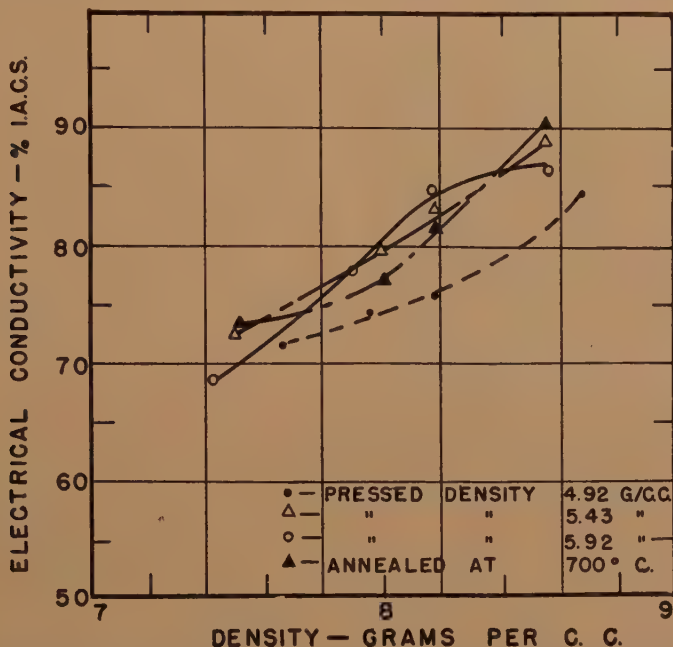


FIG. 8.—ELECTRICAL CONDUCTIVITY AS A FUNCTION OF THE REPPRESSED DENSITY OF ELECTROLYTIC COPPER-POWDER COMPACTS PRESSED TO VARIOUS DENSITIES, SINTERED ONE HOUR IN HYDROGEN AT 975°C. AND REPPRESSED.

The direct relationship of hardness versus density, after sintering and repressing, is seen in Fig. 6. The influence of the pressed density before sintering is noteworthy. The greater amount of cold-working received by the samples of lower initial density results in a higher final hardness when repressed to identical densities.

From an examination of Fig. 7 it is evident that the initial (pressed) density before sintering and repressing has a drastic influence upon the ultimate tensile strength. With decreasing initial (pressed) density, the ultimate tensile strength materially increases. Referring to Fig. 6, it will be seen that the differences in hardness do not indicate the wide spread in tensile strength values of the different specimens recorded in Fig. 7.

lowest electrical conductivity, caused probably by the greater amount of cold-working necessary to repress it to a given density.

Fig. 9 reveals the structure of a pressed, sintered and repressed copper compact at a magnification of 250 times. The grain size is small and no large voids are present.

Summarizing the work on the copper-powder compact series, it may be said that the choice of the initial pressed density will be governed primarily by the physical properties concomitant with the initial pressed density.

HOT-PRESSING OF COPPER POWDER

The simultaneous application of heat and pressure to metal powders in the preparation of compacts offers interesting

possibilities,¹ but is seriously handicapped by early failure of the dies and the consequent accompanying expense. Generally, hot pressing is conducted at a temperature

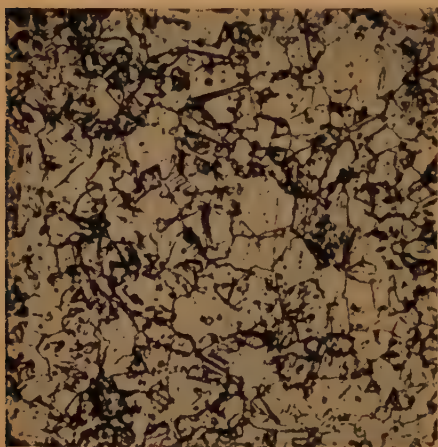


FIG. 9.—ELECTROLYTIC COPPER POWDER COMPACT. $\times 250$.

slightly in excess of the recrystallization temperature of the metal powder or powders under consideration. The generally recognized advantages incident to hot pressing are those of high physical property values coincident with low applied pressure. In certain instances, physical properties may be obtained which are impossible to attain in any other way.

Pressing within the temperature range of 25° to 600°C. indicated that optimum values of density and hardness were obtained at temperatures in the neighborhood of 400°C. A series of tests at this temperature was conducted, the results of which are illustrated in Figs. 10, 11, and 12. Fig. 10 indicates the increase in density with compacting pressure and confirms the data previously reported by Goetzl. The density curve is almost at its maximum at a pressure of about 40 tons per sq. in. and increases only slightly by a further increase in pressure to 65 tons per sq. in. Fig. 11 shows the relationship of hardness

versus density. The hardness values of 65 to 72 Rockwell B in hot-pressed copper compacts with a density of 8.75 to 8.8 grams per c. c., or 97.5 per cent of the theoretical value of 8.93 grams per c. c., are higher than can be obtained in cold-worked wrought copper.

Another interesting characteristic is that the annealing temperature of hot-pressed copper compacts is higher than that of cold-worked commercially pure copper, as shown in Fig. 12. There is very little loss in hardness up to an annealing temperature of 300°C. For comparison, the softening of hard-drawn tough-pitch copper having an initial hardness of 46 to 51 Rockwell B, is plotted in Fig. 12.

HEAT-TREATABLE COPPER-BASE COMPACTS

A series of compositions was studied to investigate the susceptibility of precipitation hardening copper-base compacts to heat-treating after pressing, sintering and repressing. The following raw materials were employed:

Copper powder, 150 mesh
 Nickel powder, 325 mesh
 Manganese powder, 325 mesh
 Cobalt powder, 325 mesh
 Copper-phosphorus alloy powder (15 per cent phosphorus), 325 mesh
 Chromium powder, 150 mesh
 Tin powder, 150 mesh
 Titanium-hydride, 200 mesh
 Beryllium-nickel alloy powder, 150 mesh
 Beryllium-cobalt alloy powder, 150 mesh
 Silicon powder, 325 mesh

Mixtures of metal powders were made of the proportions shown in Table 2 and blended in a ball mill for 8 hours.

GENERAL EXPERIMENTAL PROCEDURE

1. The first step was the compacting of small test buttons of each powder mix. The compacted test buttons were sintered, repressed, solution-treated and aged in

¹ References are at the end of the paper.

accordance with procedures listed in Table 3. The results of this processing showed that all the alloys listed in Table 2 responded to heat-treatment in varying degrees.

TABLE 2.—*Copper-base Alloy Compositions Used for Age-hardening Tests*
PER CENT

Sample Number	Nickel	Chromium	Phosphorus	Beryllium	Other	Copper
L-1503	1.00		0.25			Balance
L-1504	2.00		0.50			Balance
L-1505			0.25		0.75 Mn	Balance
L-1506			0.15		0.50 Mn	Balance
L-1507	4.00				4.00 Sn	Balance
L-1508	5.00				8.00 Sn	Balance
L-1509		3.00	0.50			Balance
L-1510		3.00	0.10			Balance
L-1511		3.00	0.10		0.5 TiH ₂	Balance
L-1512			0.50		2.0 Co	Balance
L-1271*	2.5			0.5		Balance
L-1271-A*	2.5			0.5		Balance
L-1272	3.00			0.5	0.5 Si	Balance
L-1293*				0.5	2.5 Co	Balance

* Prealloyed powders of cobalt and beryllium, or nickel and beryllium were used.

2. The second step was the compacting of small test bars on which the electrical conductivity could be measured.

TABLE 3.—*Fabricating and Heat-treating Procedures for Precipitation-hardening Copper-base Compacts*

Alloy Number	Pressing Pressure, Tons per Sq. In.	Sintering Temperature, Deg. C.	Sintering Time, Min.	Repressing Pressure, Tons per Sq. In.	Quenching Temperature, Deg. C.	Aging Temperature, Deg. C.	Aging Time, Hr.
L-1503	30	975	60	40	975	450	16
L-1504	30	975	60	40	975	450	16
L-1505	30	975	60	40	975	450	16
L-1506	30	975	60	40	975	450	16
L-1507	20	850	60	40	825	310	16
L-1508	20	850	60	40	825	310	16
L-1509	30	975	60	40	975	450	16
L-1510	30	975	60	40	975	450	16
L-1511	30	975	60	40	975	450	16
L-1512	30	975	60	40	975	450	16
L-1271	40	975	30	60	950	450	16
L-1271-A	40	975	30	60	875	450	16
L-1272	40	975	30	60	950	450	16
L-1293	40	975	30	60	975	450	16

Sintering and quenching atmospheres, hydrogen.
Aging atmosphere, air.

3. The third step was the processing of compacts of sufficient size to allow the machining of standard 0.505-in. diameter tensile test specimens. The pressures used

in pressing and repressing were of sufficient magnitude to produce a final density equal to 95 per cent that of the theoretical density for each alloy. It was necessary to carry out all high temperature heat-treating operations (sintering and solution) in a hydrogen atmosphere. If either of these treatments was done in air, the alloys would not respond properly to the precipitation treatment because of the oxidation of all or a major portion of the precipitating constituents.

EFFECT OF PRECIPITATION-HARDENING ON THE PHYSICAL AND ELECTRICAL PROPERTIES OF COPPER-BASE COMPACTS

The physical and electrical properties of the alloys listed in Table 2 are tabulated in Table 4.

Tensile data were determined only on the more promising alloy compositions. Table 4 indicates that manganese-phosphorus and nickel-tin additions to copper did not produce appreciable precipitation-hardening effects. Promising results were obtained with the addition of nickel-phos-

phorus, chromium, cobalt-phosphorus, and the nickel-beryllium and cobalt-beryllium alloy powders. The highest tensile properties were obtained with the copper-

cobalt-beryllium compact L-1293. The greatest ductility after complete heat-treatment was noted in sample L-1512.

The results of Krouse rotating beam fatigue tests on alloy L-1511 are shown in S-N curve in Fig. 13 and indicate a fatigue strength of 20,000 lb. per sq. inch.

residual oxygen either remained or was otherwise admitted into the furnace and combined with the beryllium at the surface of the compact.

Detailed studies of the aging characteristics did not reveal any phenomena radically different from those of wrought

TABLE 4.—Physical Properties

Alloy Number	Ultimate Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Electrical Conductivity as Solution Treated, Per Cent I.A.C.S.	Electrical Conductivity after Aging, Per Cent I.A.C.S.	Hardness as Re-pressed, Rockwell	Hardness as Solution Treated, Rockwell	Hardness as Aged, Rockwell
L-1503, Ni-P-Cu.....	45,000	4	22.3	30.0	22-B	25-F	20-B
L-1504, Ni-P-Cu.....			21.0	40.0	19-B	36-F	53-B
L-1505, Mn-P-Cu.....			24.4	44.1	33-B	45-F	14-B
L-1506, Mn-P-Cu.....			32.2	55.6	44-B	26-F	44-F
L-1507, Ni-Sn-Cu.....			11.7	12.8	42-B	30-B	35-B
L-1508, Ni-Sn-Cu.....	48,000	7	7.25	8.4	46-B	15-B	40-B
L-1509, Cr-P-Cu.....						38-F	53-F
L-1510, Cr-P-Cu.....			32.2	64.3	35-B	38-F	51-B
L-1511, Cr-P-TiH ₂ -Cu.....			33.5	69.1	38-B	42-F	68-B
L-1512, Co-P-Cu.....			28.5	43.4	30-B	28-F	39-B
L-1271, Ni-Be-Cu.....	52,000	7		61.0	35-B		72-B
L-1271-A, Ni-Be-Cu.....	39,400	5		52.0	35-B		60-B
L-1272, Ni-Be-Si-Cu.....	61,200	2.5		35.5	35-B		80-B
L-1293, Co-Be-Cu.....	78,200	3.1		41.0	35-B		85-B

Precipitation-hardening effects depend on the solution of the addition agents in the copper matrix. Time, temperature, particle size, and type of particle are contributing factors.

In alloy L-1293 it was found by chemical analysis that the finer particles of the cobalt-beryllium alloy contain a much higher percentage of the beryllium than do the larger particles. Because of the fineness of the particle size and excess beryllium content, it has been found that minus 325-mesh cobalt-beryllium alloy goes into solution better than the plus 325-mesh powder.

The alloy L-1293 was susceptible to the formation of a soft shell completely encasing the compact, which was caused by the partial oxidation of the beryllium for a depth as great as $\frac{1}{16}$ in. Even though the hydrogen was purified by passing it over hot copper and subsequently dried by passing it through a moisture absorbent,

alloys. It was noticed, however, that the compositions under investigation had a decreased tendency toward overaging. The alloy L-1293, for instance, retained a hardness of 45 to 50 Rockwell B after the fully aged compact was subjected to a one hour anneal at 725°C.

The heat-treated compacts of copper-nickel-beryllium (L-1271) softened at considerably lower temperatures, a severe drop in hardness occurring at 500 to 525°C., after a one-hour anneal. The temperature at which softening occurred could be raised about 100°C. by the addition of silicon (L-1272).

MICROSCOPICAL EXAMINATION

Cross sections cut from the tensile specimens of alloys L-1504, L-1510, L-1511 and L-1512 were examined microscopically.

Alloy L-1504 (nickel-phosphorus-copper) had a large, well-defined grain structure,

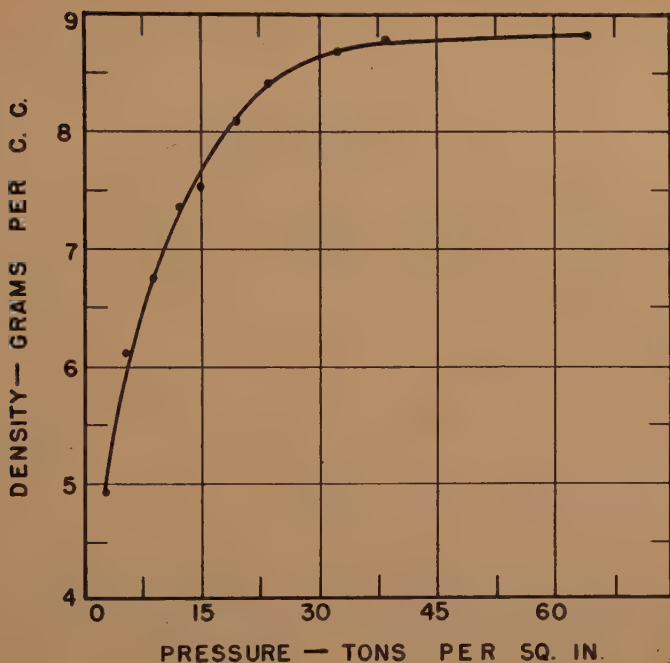


FIG. 10.—DENSITY OF ELECTROLYTIC COPPER-POWDER COMPACTS HOT PRESSED AT 400°C. ELECTROLYTIC COPPER POWDER MINUS 150 MESH.

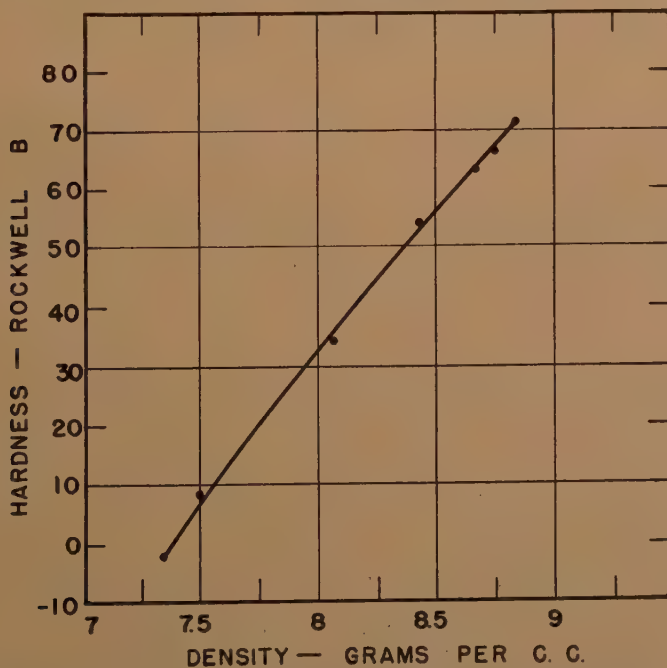


FIG. 11.—HARDNESS OF ELECTROLYTIC COPPER COMPACTS HOT PRESSED AT 400°C. TO VARIOUS DENSITIES.

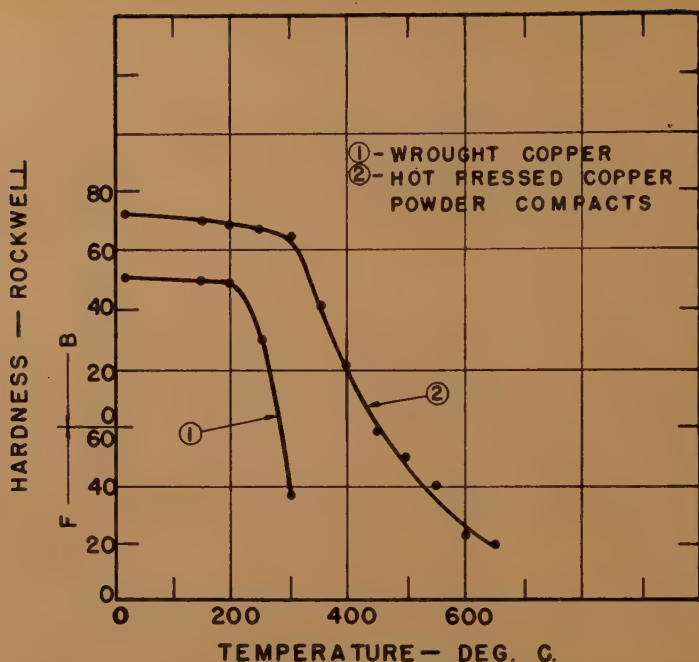


FIG. 12.—COMPARISON OF ANNEALING CURVES OF COLD-DRAWN WROUGHT COPPER AND HOT-PRESSED ELECTROLYTIC COPPER-POWDER COMPACTS PRESSED AT 400°C. AT A PRESSURE OF 65 TONS PER SQ. IN. SPECIMENS HEATED ONE HOUR AT EACH TEMPERATURE.

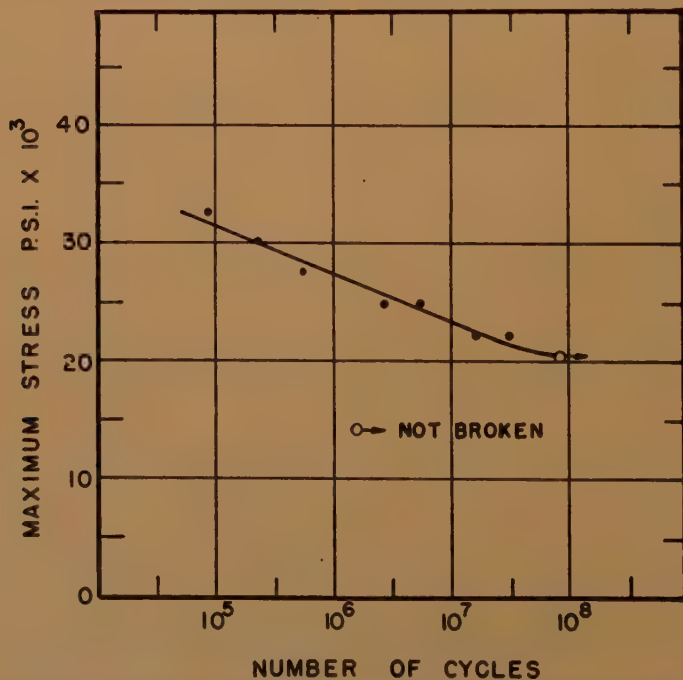


FIG. 13.—S-N CURVE OF SAMPLE L-1511 FABRICATED IN ACCORDANCE WITH PROCEDURE SHOWN IN FIGURE 15.

with excess phosphide in the grain boundaries possibly caused by incipient fusion as seen in Fig. 14. The voids were small and well distributed through the sample.

and oxidation. A typical structure is given in Fig. 15.

Alloy L-1511 (chromium-phosphorus-titanium hydride-copper) had a small, well-

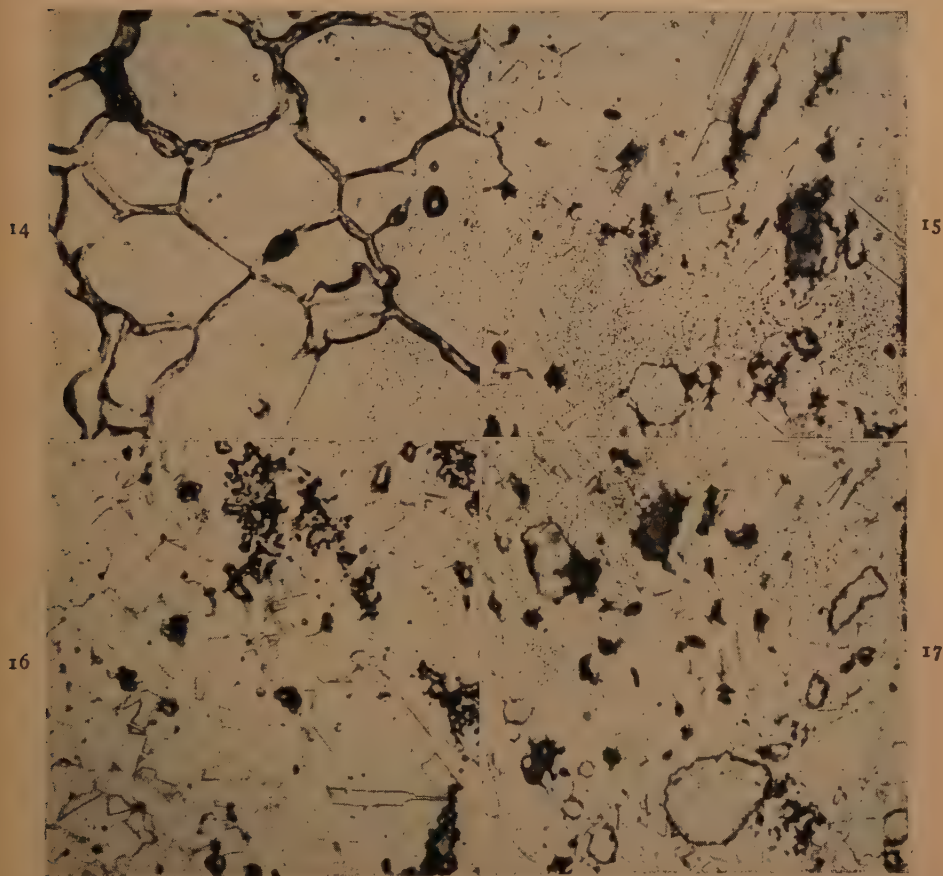


FIG. 14.—ALLOY L-1504 (2 PER CENT Ni; 0.5 PER CENT P; BALANCE Cu). ETCHANT: $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$. $\times 300$.

FIG. 15.—ALLOY L-1510 (3 PER CENT Cr; 0.1 PER CENT P; BALANCE Cu). ETCHANT: $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$. $\times 300$.

FIG. 16.—ALLOY L-1511 (3 PER CENT Cr; 0.1 PER CENT P; 0.5 PER CENT TiH_2 ; BALANCE Cu). ETCHANT: $\text{NH}_4\text{OH}_2 + \text{H}_2\text{O}$. $\times 300$.

FIG. 17.—ALLOY L-1512 (2 PER CENT Co; 0.5 PER CENT P; BALANCE Cu). ETCHANT: $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$. $\times 300$.

Alloy L-1510 (chromium-phosphorus-copper) had a somewhat irregular grain structure showing extensive twinning. Only a portion of the chromium had gone into solution. Around each free particle of chromium there was evidence of diffusion

defined structure. The titanium hydride apparently produced a cleaner material relatively free from oxidation, as evidenced by Fig. 16.

Alloy L-1512 (cobalt-phosphorus-copper) had a structure similar to that of alloy

L-1510. The presence of inclusions and of oxidation is evident from Fig. 17.

COPPER-BASE COMPACTS CONTAINING PHOSPHORUS

Because of the formation of a soft shell or layer on copper-alloy compacts con-

excellent physical and electrical properties can be obtained with age-hardening compositions containing chromium, cobalt and beryllium, or nickel and beryllium. The addition of small percentages of phosphorus and titanium hydride are beneficial in such alloys.

TABLE 5.—*Effect of Phosphorus on the Surface Hardness of Beryllium-bearing Copper-base Compacts*

	Alloy			
	A	B	C	D
Composition, per cent				
Cobalt.....	2.5	2.5		
Beryllium.....	0.72	0.72	0.32	0.32
Nickel.....			1.8	1.8
Phosphorus.....	0.19	0.27	0.22	0.3
Copper.....	Balance	Balance	Balance	Balance
Density, grams per c.c., after pressing at 30 tons per sq. in....	6.7	6.7	6.8	6.8
Sintered 1 hr. in hydrogen at 975°C. and quenched				
Hardness,* Rockwell.....	72-F	65-F	26-F	35-F
Density, grams per c.c.....	7.1	7.1	7.2	7.2
Repressed at 60 tons per sq. in.				
Hardness,* Rockwell.....	65-B	67-B	50-B	53-B
Density, grams per c.c.....	8.6	8.2	8.5	8.5
Hardness, Rockwell, after aging 8 hr. at 450°C.				
At surface.....	91-B	93-B	76-B	84-B
0.015 in. below surface.....	95-B	95-B	81-B	86-B
0.030 in. below surface.....	95-B	94-B	80-B	86-B
0.060 in. below surface.....	96-B	95-B	81-B	86-B

* Hardness at surface.

taining beryllium, even though the compacts were sintered in relatively pure hydrogen, attempts were made to eliminate or decrease the thickness of this layer by the addition of phosphorus.

Four alloys were studied, two containing copper, cobalt, beryllium and phosphorus, and two containing copper, nickel, beryllium and phosphorus. The results shown in Table 5 indicate:

1. The addition of approximately 0.2 to 0.3 per cent phosphorus greatly reduces or retards the formation of a soft shell.

2. Phosphorus additions within the range tested do not adversely affect the precipitation hardening characteristics.

SUMMARY

Copper compacts were studied and a preliminary investigation indicates that

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2. W. Trzebiatowski: Ueber Warmpressversuche an Hochdispersen Metallpulvern. *Ztsch. phys. Chem.* (1934) **A-160**, 91.
3. R. Kieffer and W. Hotop: Comparative Properties of Sintered vs. Cast Metals and Alloys. *Kolloid Ztsch.* (1943) **104**, (2-3) 208.

DISCUSSION

This discussion refers also to the following paper, beginning on page 548.

(*Frances Hurd Clark presiding*)

M. G. CORSON.*—Figs. 6 and 7 (first paper) show the effects of the compacting and sintering plus additional compacting on the density and hardness or tensile strength, respectively.

* Metallurgical Consultant, New York, N. Y.

The density-hardness curves are not open to criticism, but those of density-strength look suspicious. I cannot imagine that a compact of electrolytic copper might possess a tensile strength of 61,000 lb. per sq. in. for a density of 8.7 when hard-rolled copper with a density of 8.85 and over does not reach that figure.

2. Fig. 8 too arouses doubt. Why should a test bar with a density of 8.7 have a conductivity of 84 per cent? A loss of 16 per cent in conductivity cannot be due to a porosity of 2.7 per cent. The assumption that a greater amount of cold-work used could account for this loss of conductivity is not based on facts. Cold-work does not reduce the conductivity of sound wrought copper by more than 2 per cent, and it is a badly cupped copper wire that has a conductivity of 96 per cent.

3. The formation of a soft shell around *all* copper-base heat-hardenable alloys containing silicides or beryllides is not caused by the oxidation of silicon or beryllium. If this were so, the soft shell would carry either silica or a silicate and it would be far more pronounced in alloys of the Everdur and the beryllium-copper type, but it never occurs in the latter. That soft shell caused me much worry 20 years ago, when I originated the heat-hardenable alloys of copper with silicides or beryllides. But it is not due to the oxidation, which could be prevented—merely to a migration of silicon toward the deeper layers of any sample. The action of phosphorus consists in the reduction of the solubility of silicon and in this manner inhibits its tendency to migrate.

In order to obtain Cu-Ni-Si compacts for bearings, the authors sintered the first compacts for an hour in a hydrogen atmosphere and certainly had to wait till the latter would cool in the same atmosphere. Would it not be more rational to *melt* the alloy and execute the articles needed by the methods of precision casting?

Table 1 of the second paper gives among others the measured values of elongation and area reduction. I used to think that the best data the metallurgist might report or accept would include elongations precise within 0.5 per cent of the original length, and area reductions precise within 2 per cent of the original area. The authors, however, report elongation figures of 0.78 and even 0.977 per cent and area reductions of 0.227 and 0.228 per

cent. I wonder what calipers were used to obtain that precision.

F. H. CLARK.*—I was interested in the remarks about rather high fatigue values for these structures, even though there is some porosity present. That seems to be a possibility with metal compacts. Even though impact values are low, the fatigue strength may be higher than in cast metals. The results of some recent fatigue tests obtained by bending strip on the Sonntag Scientific Corporation fatigue tester were as follows:

	Fatigue Limit, Lb. per Sq. In.
OFHC copper rolled and annealed.....	10,000
Electrolytic copper pressed and sintered several times to obtain absolute density.....	11,000

L. S. BUSCH.†—There are any number of things that I could say, but we do have a great deal to do. As far as the copper bar with the high tensile strength is concerned, I know that the tensile strength was there, but as to the reason for it, I am not quite sure. It is the highest one that we have ever made. We did get that straight line which leads to the high value on the curve. I am inclined to agree with the gentleman who read the comments that hydrogen probably does account for the large drop in conductivity. However, remember, porosity does affect conductivity adversely as does hydrogen. It is quite probable that the combination of the three would account for the large drop in that bar. We were able to prevent any soft shell on the copper-nickel-silicon and phosphorus alloy by surrounding it with carbon or a carbon and sand mixture during sintering, and for that reason we were fairly certain it was oxidation that caused the trouble. However, Mr. Corson does have a very good case, because silicon does migrate toward the center of the bar.

F. N. RHINES.‡—The question in my mind is whether the phosphorus is acting as a deoxidizer or whether it may itself account for the

* Metallurgist, Western Union Telegraph Co., New York, N. Y.

† P. R. Mallory & Co., Inc., Indianapolis, Ind. (Mr. Busch presented the two papers.)

‡ Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

hardness that is preserved in the shell. Do you have an opinion on that question?

L. S. BUSCH.—As I said, we were able to prevent it entirely by surrounding it with carbon and sand. We examined the surface microscopically, very carefully, and it did show what we thought was evidence of a hardening due to the phosphorus alloy. I think undoubtedly it is a factor in the prevention of the soft shell, but the author of the paper is inclined to stick to the oxidation theory.

R. P. SEELIG.—You mentioned the use of alloy powders. Did you make them by the fusion method or purchase them?

L. S. BUSCH.—I believe we purchased them.

F. V. LENEL.*—Do you have any other figures on compressive properties of this material besides the modulus of elasticity in compression—figures like yield strengths in compression?

L. S. BUSCH.—As I remember, the ultimate strength in compression ran as high as 60,000 lb. per sq. in. and the yield point was, I believe, on the order of 20,000 to 30,000 lb. per sq. inch.

F. V. LENEL.—Then, did I understand that the bearings that were prepared for the General Motors bearing testing machine were machined from blanks and had no steel backing?

L. S. BUSCH.—That is correct.

F. V. LENEL.—And finally, have you made any test on an alloy that was made by conventional methods and have you any idea whether the good bearing performance of this material might be due to its being slightly porous or whether it is merely a function of the analysis?

L. S. BUSCH.—I can tell you that the regular cast and forged material with approximately the same analysis did not have the bearing properties that this material did. We think perhaps it might be due to the hard particles—similar action to the tin in babbitt plus the porosity that makes good bearing material.

F. R. HENSEL, E. I. LARSEN and E. F. SWAZY (authors' reply).—The authors considered a tensile strength of 61,000 lb. per sq. in. quite high for a compact of electrolytic copper but could, of course, only record the actual value as

measured. Considered judgment of available literature concerning the tensile strength of hard-rolled copper and the effect of impurities upon that property makes it difficult, however, to refute the values given in the paper. Hard-rolled copper reaches a tensile strength of 70,000 lb. per sq. in. with an oxygen content on the order of 0.015 per cent. Table 1 in the first paper indicates 0.25 per cent oxygen.

If we assume, as we must, that the copper is not completely reduced during sintering in hydrogen, we can state that the residual oxygen has the effect of increasing the tensile strength. It is also well known that zinc increases the tensile strength of copper, and Table 1 indicates 0.10 per cent zinc. Contrariwise, iron in small amounts is known to exert a substantially immeasurable effect upon the physical properties of copper, other than electrical conductivity, and this element may therefore be disregarded.

The authors wish to point out that the copper compact noted as reaching a density of 8.7 grams per c.c. and a tensile strength of 61,000 lb. per sq. in. as that having the lowest initial density and, therefore, receiving the greatest amount of cold-work during repressing.

Mr. Corson's discussion implies that a copper compact test bar having a density of 8.7 grams per c.c. should not have an electrical conductivity as low as 84 per cent. The authors accede that his remarks would apply to a "pure" copper compact test bar. Attention is again directed to Table 1, wherein the chemical analysis shows an iron content of 0.25 per cent. Wyman* gives the electrical conductivity of wrought copper containing 0.1 per cent iron in solution, as 75 per cent and the effect of small amounts of zinc upon this property as nil. The only conclusion that can be fairly drawn is that a portion of the iron was precipitated from solution during cooling of the compact after sintering. Only by this device could the authors have obtained even as high a conductivity as that reported.

Admittedly, the soft-shell formation in copper-alloy compacts has not been thoroughly studied and postulates only can be advanced. Table 5 gives hardness values at various depths below the surface for cobalt-beryllium-phosphorus-copper and beryllium-nickel-phos-

* Moraine Products Division, General Motors Corporation, Dayton, Ohio.

* *General Electric Review* (1934) 123.

phorus-copper alloy compacts. In all cases, the hardness has increased to a maximum at 0.015 in. below the surface. It would seem that such an abrupt increase to maximum uniform hardness would be difficult to ascribe to a reduction in solubility of any of the other components by phosphorus. Similar results were obtained for compacts containing silicides. Oxidation, however, can be abrupt and the authors found evidence of oxidation in samples examined microscopically.

The authors believe that oxidation is at least the major cause of the soft shell effect in compacts containing easily oxidized elements.

Not only the copper-nickel-silicon compacts but all compacts were allowed to cool in hydrogen after sintering. Most compacts are still porous after sintering and it would be a fool-

hardy technician who would flout laws of metallurgy such as those governing oxidation. The authors' reason for not melting the alloy was based upon previous bearing tests of the cast and wrought alloy wherein they were unsatisfactory.

It is the practice of many metallurgists to report elongation and reduction of area as the actual value measured, regardless of their magnitude. Other metallurgists reading such reports may then exercise their considered judgment in interpreting reported values. They could be reported as round numbers (of which zero is a good example) but many engineers in presenting technical papers prefer factual data rather than the popular science type.

Micrometer calipers were used to obtain the precision noted in the paper.

Silicide-hardened Copper Compacts for Bearings*

BY F. R. HENSEL,† MEMBER A.I.M.E., E. I. LARSEN† AND E. F. SWAZY†

(Chicago Meeting, February 1945)

EXPERIENCE has indicated that hard bronzes are not suitable for bearing applications where high bearing loads and speeds are involved. It is the general practice to utilize softer materials for these purposes, such as copper, lead, silver, babbitt, lead-base alloys, and more recently aluminum-base alloys, preferably supported by a steel backing. It was the objective of the present investigation to study a new material produced by powder metallurgical methods susceptible to precipitation-hardening.

TEST MATERIALS

Preliminary tests were made with compacts containing copper, nickel and silicon in quantities sufficient to form 3 to 5 per cent nickel silicide. It was found that this type of alloy was susceptible to the formation of a soft surface shell when sintered in tank hydrogen. The depth of the shell depended on the length of sintering time and sintering temperature, and varied in thickness from a few thousandths to as much as one eighth inch. This soft shell resulted from the preferential oxidation of silicon, thereby reducing the efficiency of age-hardening by the nickel silicide compound. The body of the sintered compacts below the soft shell could be precipitation-hardened to a hardness of 70 to 85 Rockwell B, by quenching from 900°C. and age-hardening at 450°C. A

series of tests was made with various addition agents, in order to decrease the rate of preferential oxidation, and it was found that phosphorus was most beneficial in this respect. After considerable experimentation, the following nominal composition was accepted as standard: 2.4 per cent nickel; 0.8 silicon; 0.3 phosphorus; balance copper. The physical properties and certain bearing properties of this alloy are described in the present paper.

PREPARATION OF COMPACTS

Several methods of incorporating the hardening ingredient (nickel silicide) were studied. Compacts formed from copper, nickel and silicon powders were found to be inferior to those fabricated from prealloyed nickel silicide master alloys, because of the rapid oxidation of pure silicon during sintering.

The use of a prealloyed nickel silicide hardener containing 25 per cent silicon and 75 per cent nickel could be further improved by preparing a master alloy, incorporating nickel, silicon, phosphorus and copper, having the following nominal composition: 25 per cent nickel; 7 silicon; 3 phosphorus; 64 copper. This alloy is brittle in the cast condition and can be readily powdered.

SINTERING PROCEDURE

The blended powders were pressed at 25 to 40 tons per sq. in., the pressure depending on the size and shape of the compacts.

Sintering was carried out in hydrogen or cracked ammonia atmospheres at

Manuscript received at the office of the Institute Aug. 27, 1945. Issued as T.P. 1976 in METALS TECHNOLOGY, February 1946.

* U. S. Patents 2372202 and 2372203.

† Metallurgical Consultant, Chief Metallurgist, and Supervisor Metallurgical Engineering Dept., respectively, P. R. Mallory and Co., Inc., Indianapolis, Indiana.

temperatures of 1000° to 1040°C. The sintering time was approximately one hour. The linear shrinkage occurring under these conditions varied from 2 to 4 per cent. The sintered density ranged from 7.74 to 8.1 grams per cubic centimeter and the hardness in the sintered condition varied from 35 to 65 Rockwell F. The electrical conductivity ranged from 19 to 22 per cent I.A.C.S. Repressing of the compacts at 50 to 60 tons per sq. in. increased the density to 8.3 to 8.5 grams per cubic centimeter.

HEAT-TREATMENT

Optimum properties were obtained with the following heat-treatment: (1) water quench from 850°C. after a soaking in nonoxidizing atmosphere for 30 to 60 min.; (2) aging for 4 to 6 hr. at 450°C. in air.

MICROSCOPICAL INVESTIGATION

A special procedure was necessary for preparing samples for microscopical examination to prevent the removal of nickel silicide particles by the polishing operation. The following procedure was found successful:

1. Rough grind.
2. Fine grind through No. 000 emery paper.
3. Rough polish with 600-mesh aluminum oxide.
4. Fine polish on silk lap using No. 3 polishing alumina.
5. Etch with potassium dichromate.
6. Repolish on silk lap and re-etch.

Fig. 1 shows the microstructure after pressing and sintering. Free nickel silicide is evident in the grain boundaries and the darkening effect of the grains by etching also indicates that nickel silicide was precipitated within the grains. It was noted that the sintered compacts were benefited by the use of prealloyed copper, nickel, phosphorus and silicon, in that the free nickel silicide particles were noticeably smaller and the microstructure exhibited a greater uniformity than that obtained by the use of a nickel silicide and phosphorus-copper as separate powders.

Fig. 2 shows the effect of quenching. The major portion of the nickel silicide phase that was precipitated within the grains before quenching has been taken into solid solution. Also, a portion of the nickel silicide contained within the grain boundaries has gone into solution.

Fig. 3 shows the effect of aging on the microstructure. The grains were uniformly darkened as a result of submicroscopic precipitation of nickel silicide during aging. In comparing Fig. 1 with Fig. 3, the difference between the precipitation as it occurs in cooling after sintering and precipitation and as obtained during aging is evident.

Fig. 4 shows complex nickel silicide particles at a magnification of 500 diameters. The band across the particle, indicated by an arrow, had a blue-gray appearance when viewed under the microscope while the remainder of the particles were copper colored but were of a different shade than the matrix. The black areas adjacent to the particles are voids, some of which were the result of incomplete compacting, although it is believed the majority were caused by polishing. Microhardness tests were carried out to determine the hardness of the matrix and the nickel silicide particles. The bluish constituent had a hardness of 851 V.P.N. Portions of the constituent having more of a copper color had a hardness in the neighborhood of 500 V.P.N. This lower hardness undoubtedly is due to absorption of copper by the nickel silicide. In the center of a copper alloy grain in the heat-treated matrix the hardness was found to be 186 V.P.N. By conversion this compares favorably with the over-all hardness of the compacts obtained using the larger penetrator and load of a standard Rockwell hardness tester.

PHYSICAL PROPERTIES

Coefficient of Expansion.—Fig. 5 shows an expansion curve, obtained on A.S.T.M. type of equipment, of a compact after

FIG. 1.



FIG. 2.

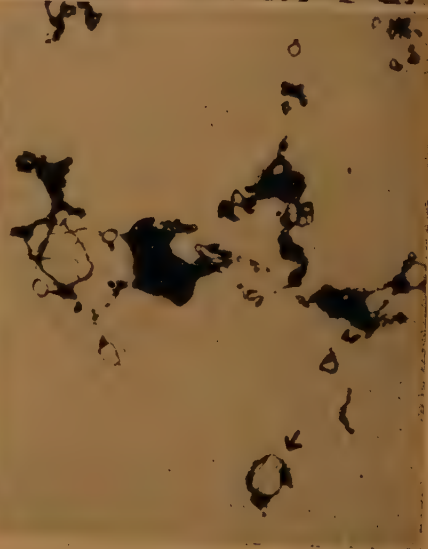
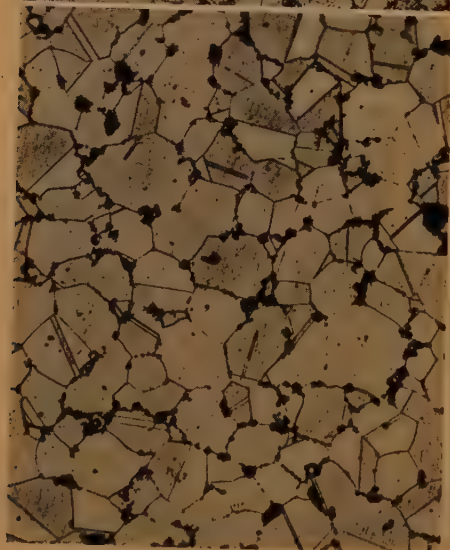
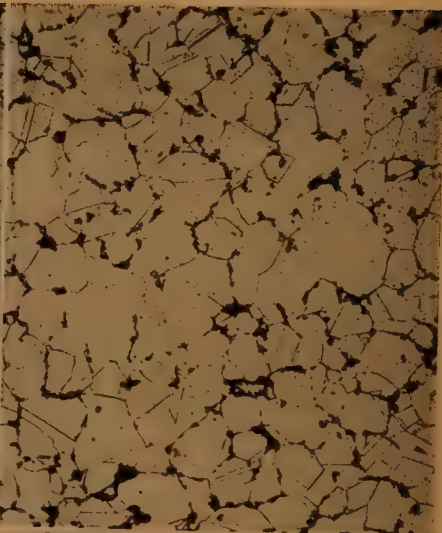


FIG. 3.

FIG. 1.—MICROSTRUCTURE AFTER PRESSING AND SINTERING.
Sample No. D-1206-A. $\times 75$.

FIG. 2.—MICROSTRUCTURE AFTER QUENCHING.
Sample No. D-1206-E. $\times 75$.

FIG. 3.—MICROSTRUCTURE AFTER AGING.
Sample No. D-1206-C. $\times 75$.

FIG. 4.—MICROSTRUCTURE OF NICKEL-SILICIDE PARTICLES.
Sample No. D-1206-F. $\times 500$.

quenching from 850°C. and aging 4 hr. at 450°C. The specimen had a hardness of 75 to 80 Rockwell B and a density of 8.3 grams per cubic centimeter. An incon-

were obtained. The copper powder used in the preparation of sample D-1206 was minus 300-mesh as compared with minus 200-mesh copper powder used in the

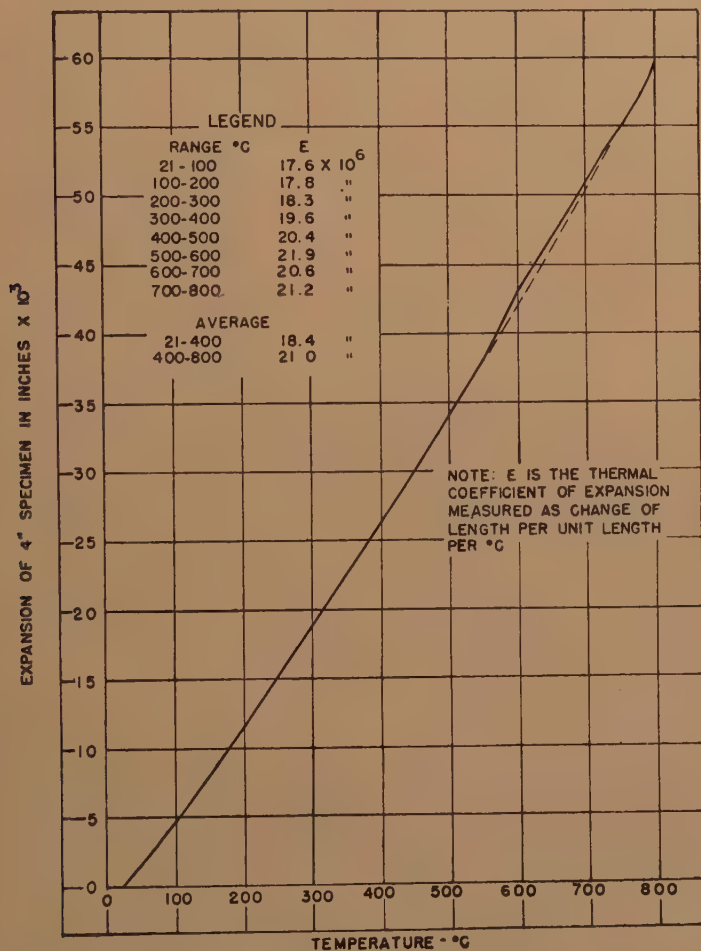


FIG. 5.—THERMAL EXPANSION OF PRESSED, SINTERED, QUENCHED AND AGED COPPER-NICKEL SILICIDE COMPACT.

sistency in the expansion curve is apparent at temperatures between approximately 550° and 700°C. This inconsistency was noted in a number of different specimens.

Tensile Properties.—Tensile properties after heat-treatment are listed in Table 1 and the dimensions of the test piece are shown in Fig. 6. Ultimate tensile-strength values of 50,000 to 60,000 lb. per sq. in.

preparation of all other specimens. There were indications that the fineness of the copper powder has a direct bearing on the density and tensile properties because of its greater reactivity to diffusion alloying during the sintering operation.

Compressive Strength.—Tests for the determination of compressive strength were carried out at Battelle Memorial

Institute, by R. W. Dayton and E. M. Simonds. A special fixture was built to eliminate all nonaxial loads during the tests. This work indicated that compression

in diameter and 3 in. long. The contact surfaces of each specimen were ground as nearly perpendicular to the axis and parallel to each other as possible.

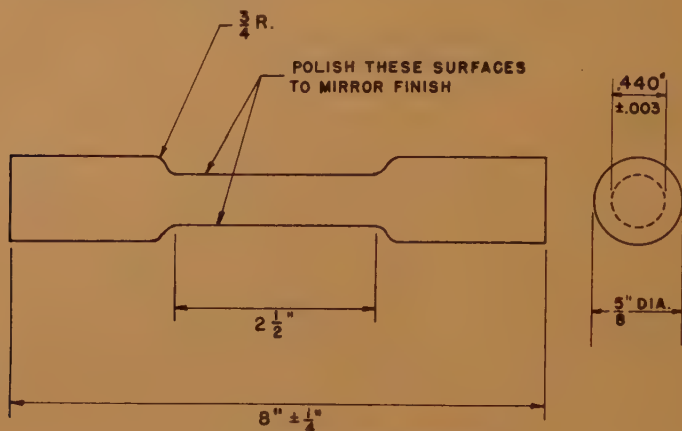


FIG. 6.—TENSILE-TEST SPECIMEN.

tests are highly sensitive to misalignment but that when great care is taken sintered materials obeyed Hooke's law. The fixture used is shown in Fig. 7. The plunger is an exceptionally close fit in the hole, to eliminate the influence of nonaxial forces. The spherically seated pads above the plunger and below the specimen helped to obtain good initial alignment. Two Tuckerman optical extensometers mounted 180° apart were used on each specimen. Both employ a 1-in. gauge length but have different calibration factors, one being readable to an accuracy of 4 microinches and the other to 8 microinches. The specimens used were approximately $1\frac{5}{16}$ in.

A series of test runs indicated that there is a straight-line relationship between density and modulus of elasticity in compression as shown in Fig. 8.

Fatigue Tests.—The improvements made by the use of prealloyed powders were most strongly reflected in fatigue tests. Fig. 9 shows the *S-N* curve of heat-treated compacts made from a mixture of copper, nickel, silicon and phosphorus copper powders, while Fig. 10 shows the *S-N* curve for heat-treated compacts made from copper and prealloyed powders. The endurance limit of the material illustrated in Fig. 9 is in the neighborhood of 10,000 per sq. in. while the endurance

TABLE 1.—*Tensile Properties after Heat-Treatment*

Sample No.*	Specimen No.	Proportional Limit, Lb. per Sq. In.	Elastic Limit, Lb. per Sq. In.	Ultimate Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent per In.	Reduction of Area, Per Cent	Density, Grams per C.C.
D-1205-C	1	14,400	28,800	49,200	0.977	0.227	7.96
D-1205-C	2	16,700	34,100	50,900	1.37	0.687	7.74
D-1206-C	5	13,100	38,100	55,600	1.37	0.228	8.34
D-1205-E	3	7,900	36,700	61,500	2.34	1.14	8.28
D-1205-E	4	9,200	28,800	52,250	0.78	0.228	8.44

* D-1205-C and D-1206-C, sintered, water-quenched from 850°C., aged 5 hr. at 450°C. D-1205-E, sintered, repressed, water-quenched from 850°C., aged 5 hr. at 450°C.

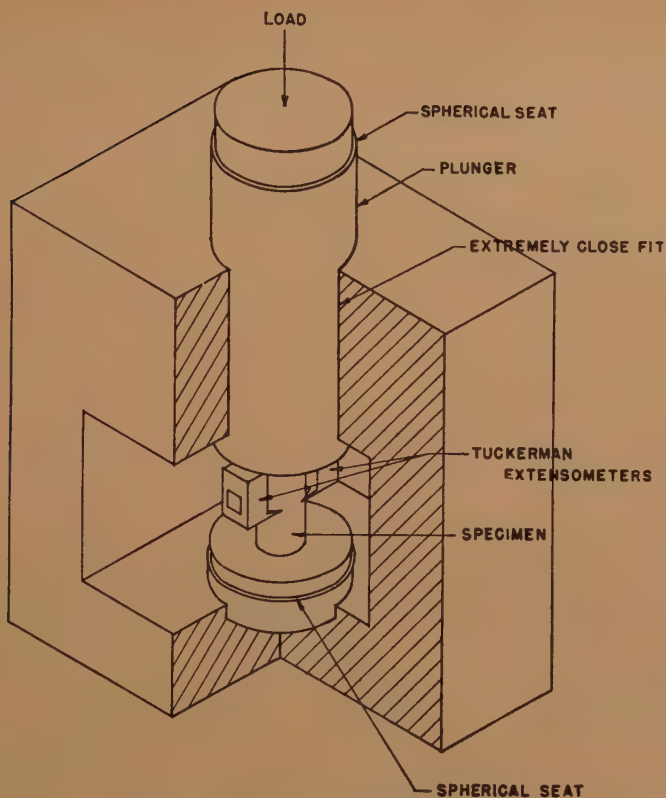


FIG. 7.—FIXTURE FOR COMPRESSION TEST.

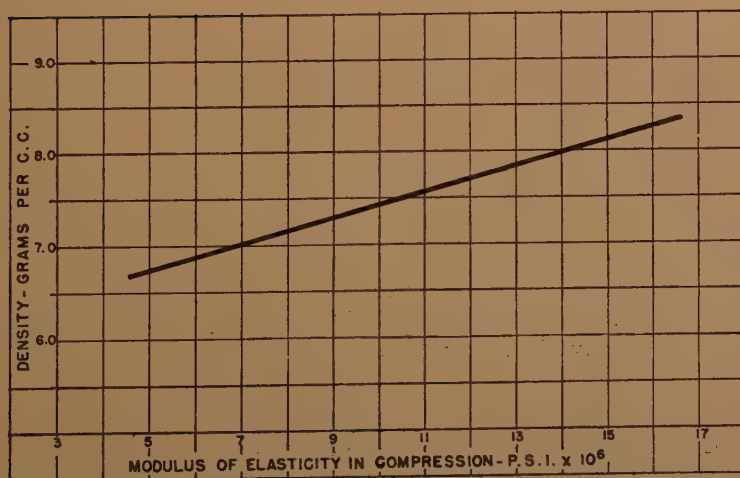


FIG. 8.—DENSITY VS. MODULUS OF ELASTICITY IN COMPRESSION FOR SILICIDE-HARDENED COPPER COMPACTS.

limit of the material illustrated in Fig. 10 is 17,500 per sq. in., which represents a 75 per cent increase over that of compacts made from elemental powders.

aged. The material had a Rockwell B hardness of 77 to 81. This preliminary test indicated that the material was considerably more resistant to seizure than

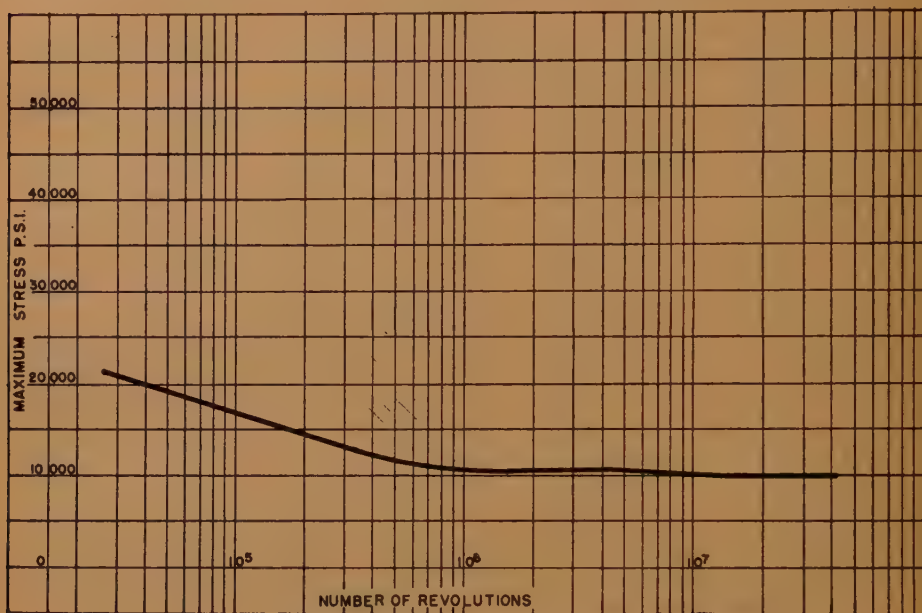


FIG. 9.—ENDURANCE TEST ON KROUSE ROTATING-BEAM FATIGUE MACHINE.

Material: Compact produced from a mixture of copper, nickel, silicon and phosphoric copper powders. Pressed at 25 tons per sq. in., sintered in H_2 at 1000° to $1025^\circ C$. Heated to $850^\circ C$. in H_2 and quenched in water. Aged for 4 hours at $450^\circ C$. in air.

ELECTRICAL CONDUCTIVITY

The electrical conductivity of sintered test pieces having a density of 8 grams per c.c. varied from 19.5 to 21 per cent I.A.C.S. After repressing at 50 tons per sq. in. to a density of 8.3 grams per cm., the conductivity ranged from 20.5 to 21.5 per cent I.A.C.S. Quenching of the repressed specimen in water from $850^\circ C$. reduced the electrical conductivity to 14.5 per cent I.A.C.S. and aging for 5 hr. at $450^\circ C$. resulted in a conductivity of 23 to 25 per cent I.A.C.S.

BEARING TESTS

Amsler seizure tests were carried out at Battelle Memorial Institute on a material that was sintered, repressed, quenched and

such alloys as copper-lead or tin bronzes. The material was then tested in the General Motors machine under conditions of considerable severity. Normally this machine simulates automotive connecting-rod service, but for these tests the load was increased about 50 per cent so that it was approximately midway between the loads of automobile and aircraft service. The bearings were machined to 2.365 in. o.d. by 1.992 in. i.d. and 1.28 in. long. The shaft on which the bearings ran was of S.A.E. 1045 steel hardened to 45 Rockwell C and ground to 1.989 in. diameter, thus giving 0.003 in. clearance over all. The roughness of the ground finish was 17 to 19 micro-inches. The test consisted of 5 hr. of wearing in and warming up and 50 hr. of

test. The speeds, loads and duration of test were as follows: 2 hr., 1725 r.p.m., 540 lb. per sq. in. 3 hr., 2130 r.p.m., 840 lb. per sq. in. 50 hr., 3550 r.p.m., 2300 lb.

CONCLUSIONS

The bearing-test results of heat-treated copper-nickel silicide compacts were most unexpected in that it was possible that so

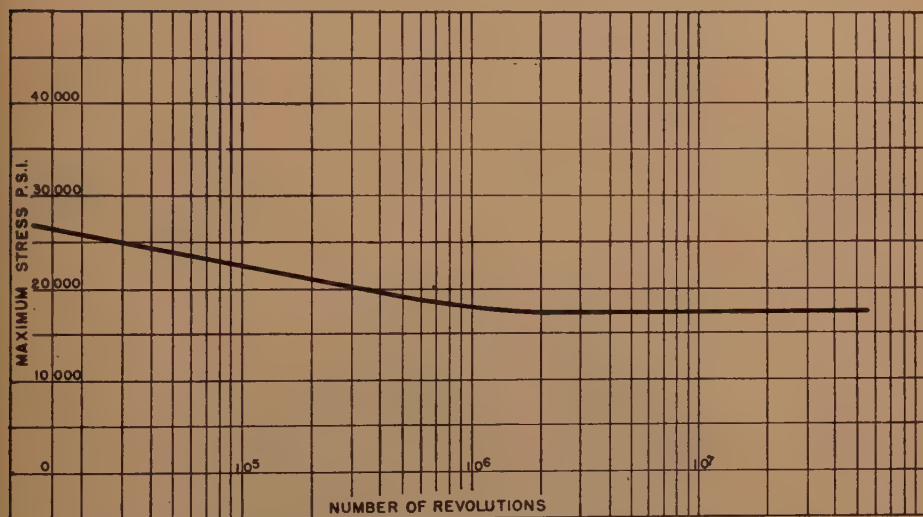


FIG. 10.—ENDURANCE TEST ON KROUSE ROTATING-BEAM FATIGUE MACHINE.

Material: Compact made from copper and prealloyed powders. Pressed at 25 tons per sq. in., sintered in H_2 at 1000° to $1025^\circ C.$ Heated in H_2 $\frac{1}{2}$ hour at $850^\circ C.$, quenched in cold water. Aged 4 hours at $450^\circ C.$ in air.

per sq. in. Two types of materials were tested, one that was sintered, quenched and aged, having a Rockwell B hardness of 35 to 40 and a density of 7.74 grams per c.c. and one that was sintered, repressed, quenched and aged, having a hardness of 75 to 80 Rockwell B and a density of 8.4 grams per c.c. The bearings ran through the test without showing distress of any sort and were in excellent condition at completion of the test. There were no signs of metal to metal contact on the bearings and very few scratches, the latter probably caused by dirt.

The shaft, too, was in good condition. Brightening was evident at the high load points, but there was little of the gouging that often occurs with copper-lead bearings on shafts that are not fully hardened.

hard a bearing could be run at such high speeds and loads and that the shaft did not show excessive wear. Further tests are under way, which, it is hoped, will throw more light on the facts discovered thus far.

ACKNOWLEDGMENTS

The authors wish to express their sincere gratitude for the assistance rendered by Dr. R. W. Dayton, of Battelle Memorial Institute, and Messrs. Lee Busch, A. S. Doty, A. M. Suggs and Miss Muriel Adams, of the Metallurgical Department of the P. R. Mallory and Co., Inc.

DISCUSSION

See page 544.

A Study of the Physical Properties and Microstructure of Sintered Steel

BY GEORGE STERN,* JUNIOR MEMBER A. I. M. E.

(Chicago Meeting, February 1946)

THE purpose of this investigation has been to study one method for making ordinary carbon steel by the powder metallurgy technique. This method con-

hydrogen-reduced and electrolytic iron powders, both containing 0.5 per cent carbon. Methods for making steel bodies by powder metallurgy have also been sug-

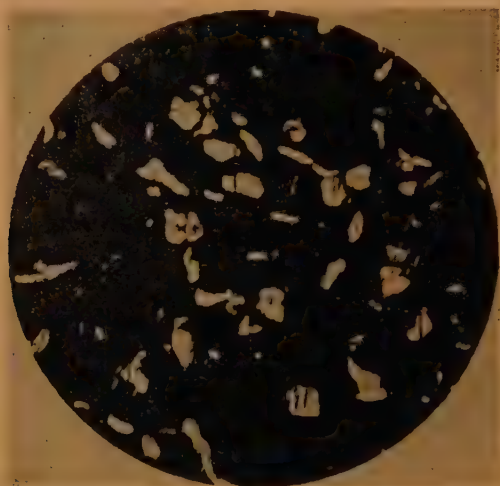


FIG. 1.—ELECTROLYTIC IRON POWDER AS POLISHED. $\times 75$.

sists of pressing and subsequently sintering an intimate mixture of iron powder and graphite in a suitable atmosphere to produce a steel. Two types of iron powder have been studied, electrolytic and reduced.

The sintering of mixtures of loose carbonyl iron and carbon black for several hours at 1000° to 1100°C . (1830° to 2010°F .), followed by forging of the resultant ingots to bars, has been studied by Offermann.¹ Trail² has reported on the properties of

gested by Goetzel,³ who recommends the addition of steel powder of well-defined carbon content to pure iron powder, and Volterra,⁴ who suggests compaction and subsequent sintering of a mixture of steel powder, iron oxide and iron powder. Additional methods for making steel bodies by powder metallurgy have been reported in the literature by Koehring,⁵ Allen,⁶ Balke,⁷ Wulff,⁸ Boegehold,⁹ and others.^{10,11,12}

It is felt that the method of pressing iron powder and graphite, as described herein, lends itself best to production because of the lubricating action of the

Manuscript received at the office of the Institute April 8, 1946. Issued as T.P. 2045 in METALS TECHNOLOGY, August 1946.

* Metallurgist, American Electro Metal Corporation, Yonkers, New York.

¹ References are at the end of the paper.

graphite powder, the low die wear and the reasonably low pressures and practical temperatures required.

iron, and this form of carbon was therefore selected for addition to the iron powder.

The properties of a typical batch of the

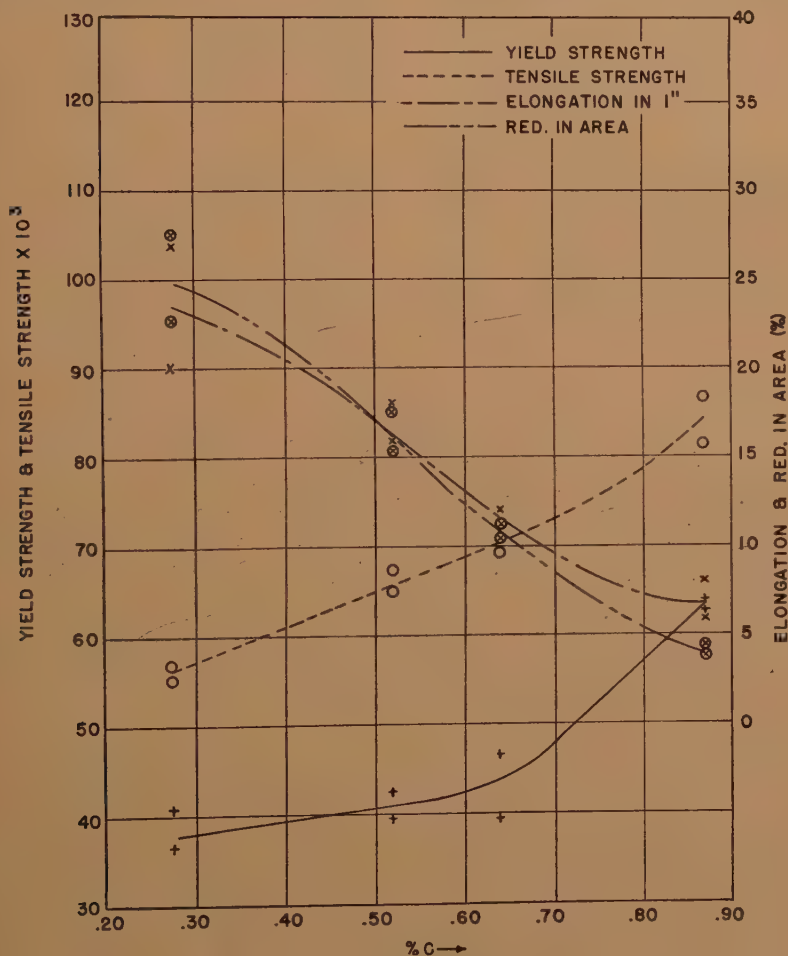


FIG. 2.—ELECTROLYTIC IRON AND GRAPHITE.
Physical properties vs. carbon content. Furnace-cooled from 2000°F.

ELECTROLYTIC IRON PLUS GRAPHITE

Raw Materials

In order to obtain the best possible results, an attempt has been made to work with the purest iron powder commercially available. Toward this end, an electrolytic powder was selected. Other investigators¹³ have found a fine graphite powder excellent for rapid diffusion into

electrolytic powder are as follows:

	PER CENT
Screen Analysis:	
+100.....	0
-100 + 140.....	7.0
-140 + 200.....	28.5
-200 + 230.....	7.5
-230 + 325.....	17.5
-325.....	39.5
Total.....	100.0

Apparent density... 3.0 grams per c.c. (varies up to 3.12)

Flow..... 26 sec. per 50 grams

Hydrogen loss, per cent:

As received..... 0.34 (varies up to 1.10)

As annealed.... 0.13 (varies up to 0.35)

Fig. 1 is a micrograph of this powder, and shows that it consists mainly of particles of irregular shapes, tending toward spheres, with few of the elongated or platelike particles typical of most electrolytic powders.

Four mixtures were studied, containing 0.40, 0.65, 0.85, and 1.05 per cent by

weight of graphite, respectively, and hereafter referred to as mixtures I, II, III and IV.

The powder was weighed out and tumbled for one hour for each mixture. No lubricant was added to the powder mixture, as the die walls were thoroughly painted with a solution of Sterotex in acetone.

Experimental Procedure and Results

As a result of preliminary investigation the following processing schedule was selected, since it was felt that the compacting pressures and temperatures were

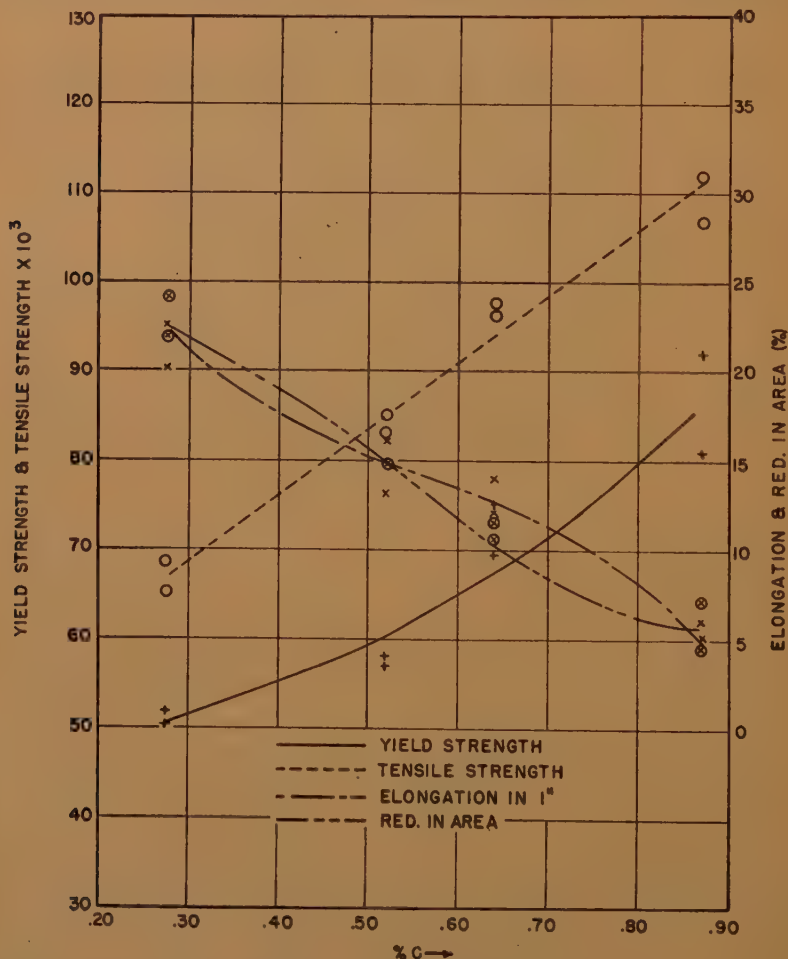


FIG. 3.—ELECTROLYTIC IRON AND GRAPHITE

Physical properties vs. carbon content. Furnace-cooled from 2000°F., oil-quenched from 1525°F. to 1575°F. Drawn at 600° to 800°F.

commercially feasible:

Press..... 50 tons per square inch
 Presinter..... 2000°F. for 15 minutes
 Repress..... 50 tons per square inch
 Resinter..... 2000°F. for 1 hour

The first sintering for 15 min. permits the carbon to react with the oxygen in the compact but does not allow for complete diffusion of the carbon. Hence our material is more susceptible to plastic deformation in the repressing operation, whereas if complete diffusion were per-

mitted, the steel formed would resist this plastic deformation.

Mixtures I to IV Sintered in Cracked Propane in Presence of Lithium Salts (Lithiated Atmosphere)

Cracked ammonia having a dew point of minus 40°C. on entering the furnace was first used as a sintering atmosphere. However, owing to opening of the front and rear doors of a push-type furnace in charging and discharging boats containing

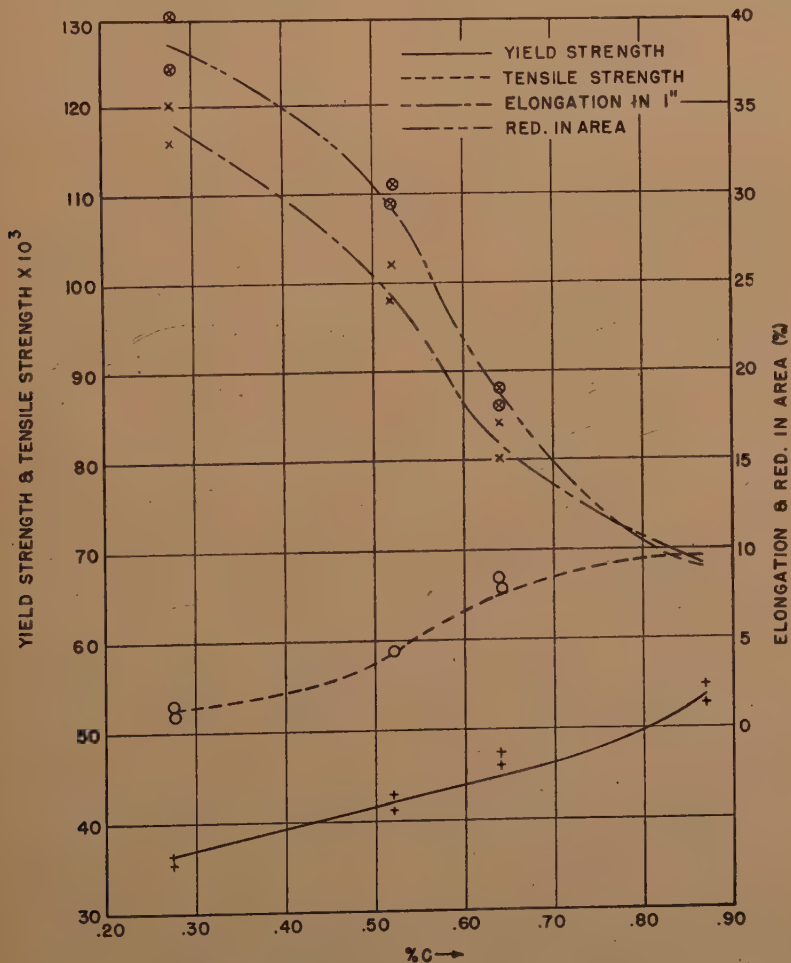


FIG. 4.—ELECTROLYTIC IRON AND GRAPHITE.

Physical properties vs. carbon content. Furnace-cooled from 2000°F., oil-quenched from 1525° to 1575°F. Drawn at 1300°F.

the samples, the dew point in the furnace was actually much higher, causing excessive decarburization.

A detailed study was therefore made

propane, and by placing lithium salts on the boat carrying the charge as well as in the lithium generator,* practically no decarburization of the charge took place.

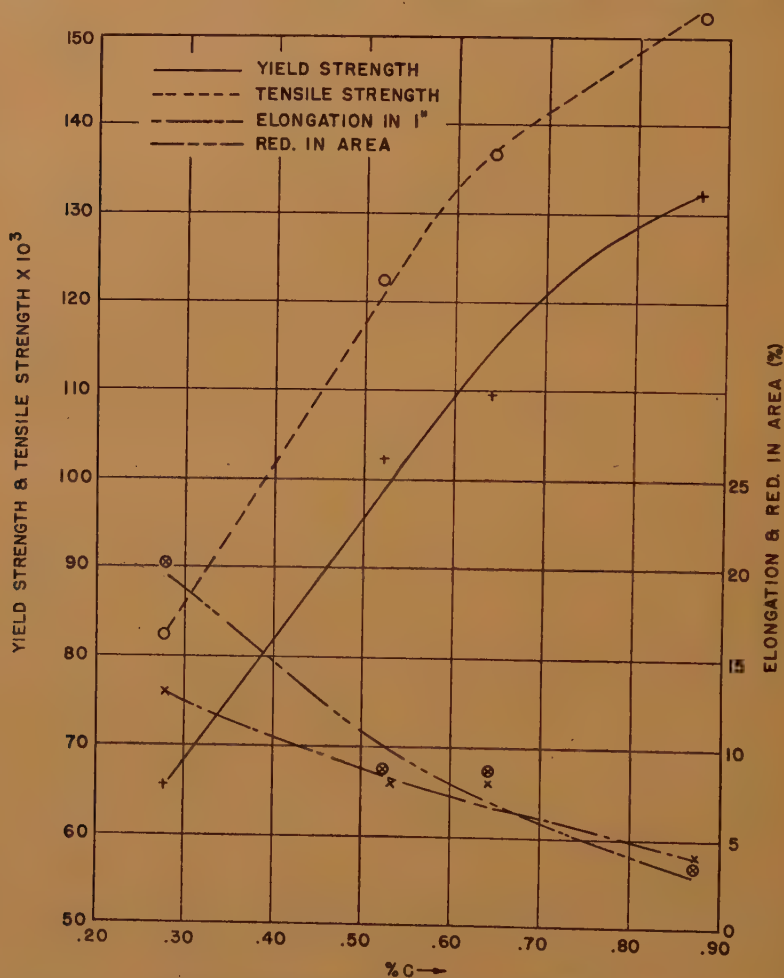


FIG. 5.—ELECTROLYTIC IRON AND GRAPHITE.

Physical properties vs. carbon content. Furnace-cooled from 2000°F., water-quenched from 1525°F. Drawn at 600°F.

on a small push-type furnace, to determine whether a cracked propane atmosphere containing lithium vapors generated from lithium salts could be adjusted to give a more closely neutral atmosphere. It was found that by using a ratio of 80 cu. ft. per hour of air to 10 cu. ft. per hour of

Table I summarizes the results using various ratios of air to propane in this furnace with mixtures I, II, III and IV pressed at 50 tons per square inch and

* The lithium generator contains lithium salts heated to 1700°F., and the cracked propane passes through the generator before entering the furnace muffle.

TABLE 1.—*Effect of Various Ratios of Air to Propane*

Mixtures Pressed at 50 Tons per Square Inch and Sintered at 2000°F. for One Hour

Air-gas Ratio	Mixture	Effect of Atmosphere
7.2/1	I	Carburized, Mm. I.2 I.5 I.5 I.0
	II	
	III	
	IV	
7.7/1	I	0.9 I.4 I.9 2.0
	II	
	III	
	IV	
8.2/1	I	Practically neutral
	II	
	III	
	IV	
8.4/1	I	Decarburized, Mm. 0.2 0.4 0.5 0.3
	II	
	III	
	IV	
10.8/1	I	I.2 I.5 I.4 I.1
	II	
	III	
	IV	

approximately $\frac{5}{8}$ in. high and a standard 3 by 0.250-in. diameter test bar with 1-in. gauge length was machined from each compact after heat-treatment for tensile testing, while a standard double Izod bar was machined for impact testing.

Four types of heat treatment were performed:

1. Samples were tested as furnace-cooled* after pressing, presintering and repressing.

2. Samples were oil-quenched from 1525° to 1575°F. and drawn at 600° to 800°F., depending on the carbon content of the sample.

3. Samples were oil-quenched from 1525° to 1575°F., depending on the carbon content, and drawn at 1300°F.

4. Samples were water-quenched from 1525°F. and drawn at 600°F.

The yield strength, tensile strength, elongation in one inch and reduction in

sintered at 2000°F. for 1 hr. In all tests lithium salts were placed on the boat as well as in the lithium generator.

All samples were single pressed in a die 3 by $\frac{5}{8}$ in. and were reversed 180° when repressed. The final compacts were

* The boat containing the charge is pushed from the hot zone at 2000°F. to a nonheated part of the muffle at room temperature. The rate of cooling is actually faster than a true furnace cool.

TABLE 2.—*Comparison of Mechanical Properties of S.A.E. and Sintered Steels^{a, b}*

Treatment	1020		1040		1060		1080	
	S.A.E.	Sin.	S.A.E.	Sin.	S.A.E.	Sin.	S.A.E.	Sin.
Furnace-cooled								
Y.P. ^b	43	37	52	40	59	42	62	57
T.S. ^b	66	55	88	61	95	69	102	79
El.....	35	25	29	21	24	13.5	20	7.5
Red. Area.....	55	27	60	22	51	12.5	48	5.5
Oil-quenched and drawn at 1300°F.								
Y.P. ^b	38	35	55	39	72	44	80	50
T.S. ^b	60	52	82	55	98	63	100	60
El.....	35	35	30	30	26	18.5	23	10.5
Red. Area.....	65	40	60	35	61	22	56	10.5
Oil-quenched and drawn at 800°F.								
Y.P. ^b	57	50	76	55	105	65	125	80
T.S. ^b	77	65	110	76	144	91	175	106
El.....	30	25	19	18	17	13.5	12	8
Red. Area.....	58	25	48	19	48	12	40	6.5
Water-quenched and drawn at 600°F.								
Y.P. ^b	80	60	95	82	110	140	129	
T.S. ^b	98	75	125	102	133	200	148	
El.....	15	15	11	10.5	7.5	12	5	
Red. Area.....	45	23	42	14.5	8	33	4	

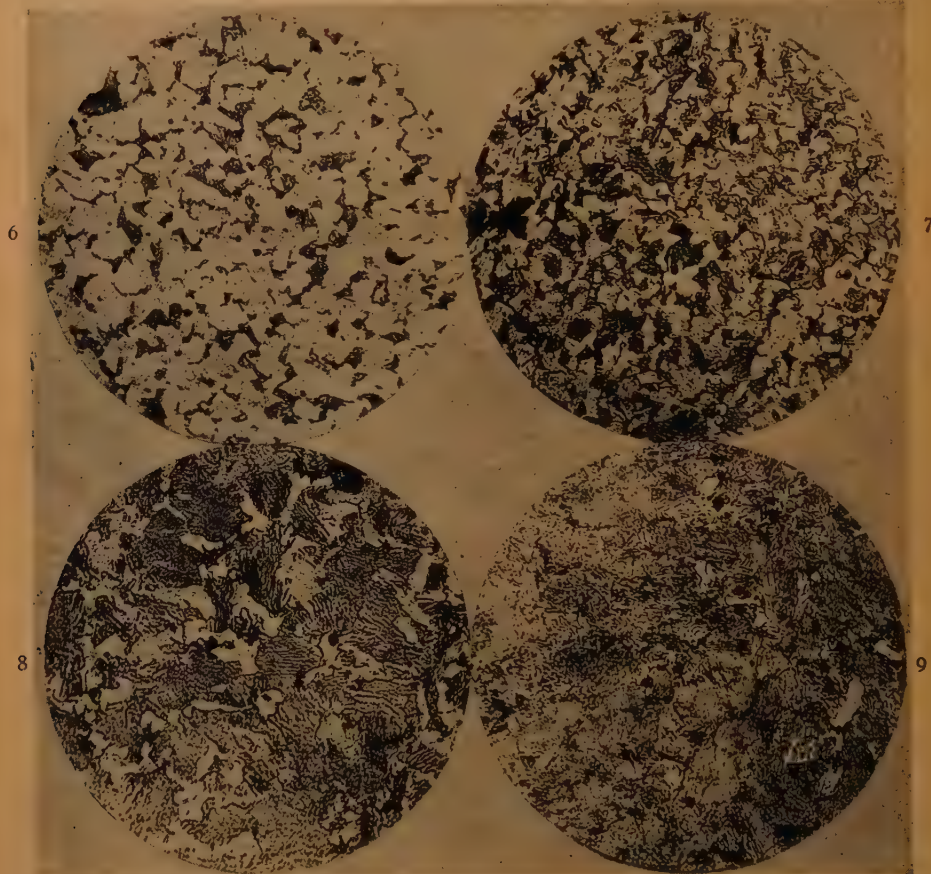
^a S.A.E. values from Alloys of Iron and Carbon¹⁶ for 1020, 1040, 1080; S.A.E. values from Metals and Alloys Data Book¹⁴ for 1060; sintered values from Figs. 2, 3, 4 and 5.

^b Yield point and tensile strength $\times 10^3$.

^c Sintered steels have a density of 93.9 to 96.2 per cent.

area are plotted versus carbon content for each heat-treatment in Figs. 2, 3, 4 and 5.

reasonably close to those of plain carbon S.A.E. steels. The values for sintered steels deviate on the low side from those of



FIGS. 6-9.—MIXTURES I, II, III AND IV AS FURNACE-COOLED FROM SINTERING TEMPERATURE.

× 200. ETCH PICRAL.

Fig. 6. Mixture I; C, 0.28 per cent.

Fig. 7. Mixture II; C, 0.52 per cent.

Fig. 8. Mixture III; C, 0.64 per cent.

Fig. 9. Mixture IV; C, 0.87 per cent.

Values were taken from these curves for 0.20, 0.40, 0.60 and 0.80 per cent carbon contents and these values are compared with data for 1020, 1040, 1060 and 1080 S.A.E. steels in Table 2.

From Table 2 and Figs. 2 to 5, inclusive, the following conclusions can be drawn:

1. Steels made from electrolytic iron and graphite powders can be treated to give yield strengths and tensile strengths

S.A.E. steels more in the higher carbon ranges (1060 and 1080).

2. The elongation values for these sintered steels approach the values obtained with plain carbon S.A.E. steels for the low and medium carbon range (0.20 to 0.40 per cent C).

In the higher carbon range (0.60 to 0.80 per cent C) the elongation values for sintered steels drop to about three fourths

or less of the corresponding values for S.A.E. steels. This can be accounted for by the increased porosity of the sintered steels as carbon content is increased. This is due to the increased resistance to deformation after presintering as the carbon content increases.

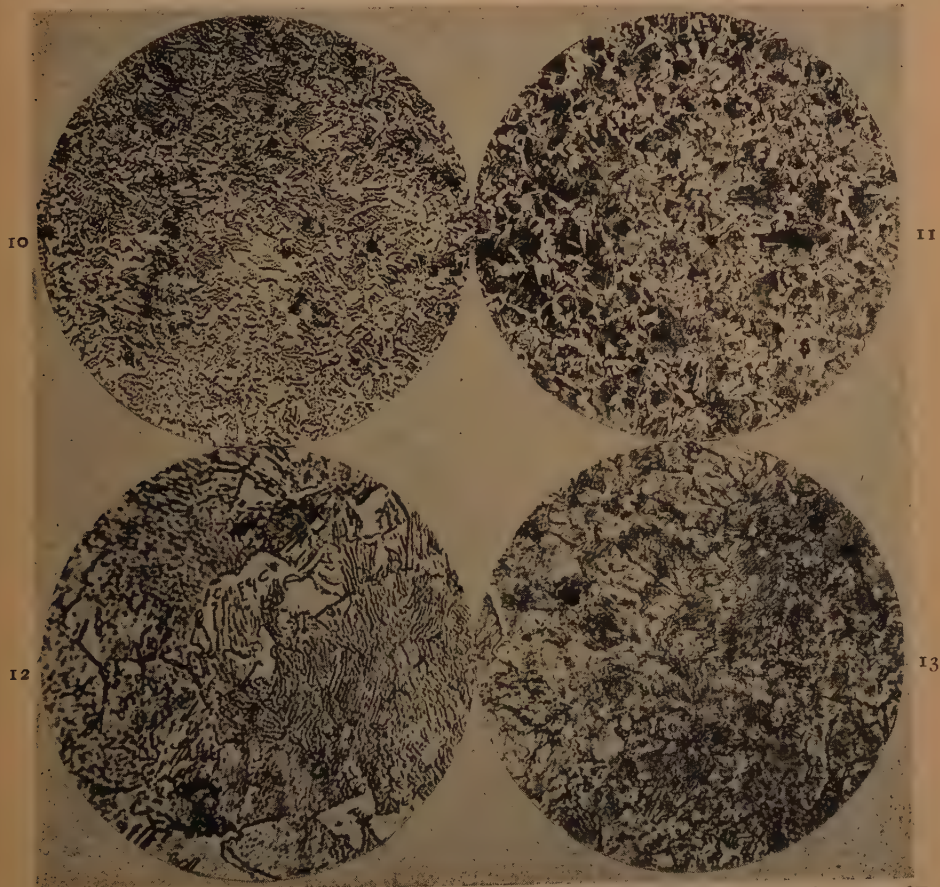
Table 3 summarizes the data on density after pressing, presintering, repressing and resintering for steel compacts made from mixtures I to IV.

3. The figures for reduction in area for the sintered steels are about half those

for the S.A.E. steels for the low and medium carbon range (0.20 to 0.40 per

TABLE 3.—*Density for Mixtures (Average of Ten Bars) Pressed, Presintered, Repressed and Resintered*

Mixture	Theoretical Density, Grams per C.C.	Average Density, Grams per C.C.	Average Density, Per Cent of Theoretical	Porosity, Per Cent
I	7.85	7.54	96.2	3.8
II	7.84	7.47	95.3	4.7
III	7.83	7.43	94.9	5.1
IV	7.82	7.33	93.9	6.1



FIGS. 10-13.—MIXTURES I, II, III AND IV FURNACE-COOLED, REHEATED TO 1525° TO 1575°F., OIL-QUENCHED, TEMPERED AT 600° TO 800°F.

Fig. 10. Mixture I; C, 0.28 per cent. $\times 200$. Etch Nital.

Fig. 11. Mixture II; C, 0.52 per cent. $\times 200$. Etch Nital.

Fig. 12. Mixture III; C, 0.64 per cent. $\times 1000$. Etch Picral.

Fig. 13. Mixture IV; C, 0.87 per cent. $\times 1000$. Etch Picral.

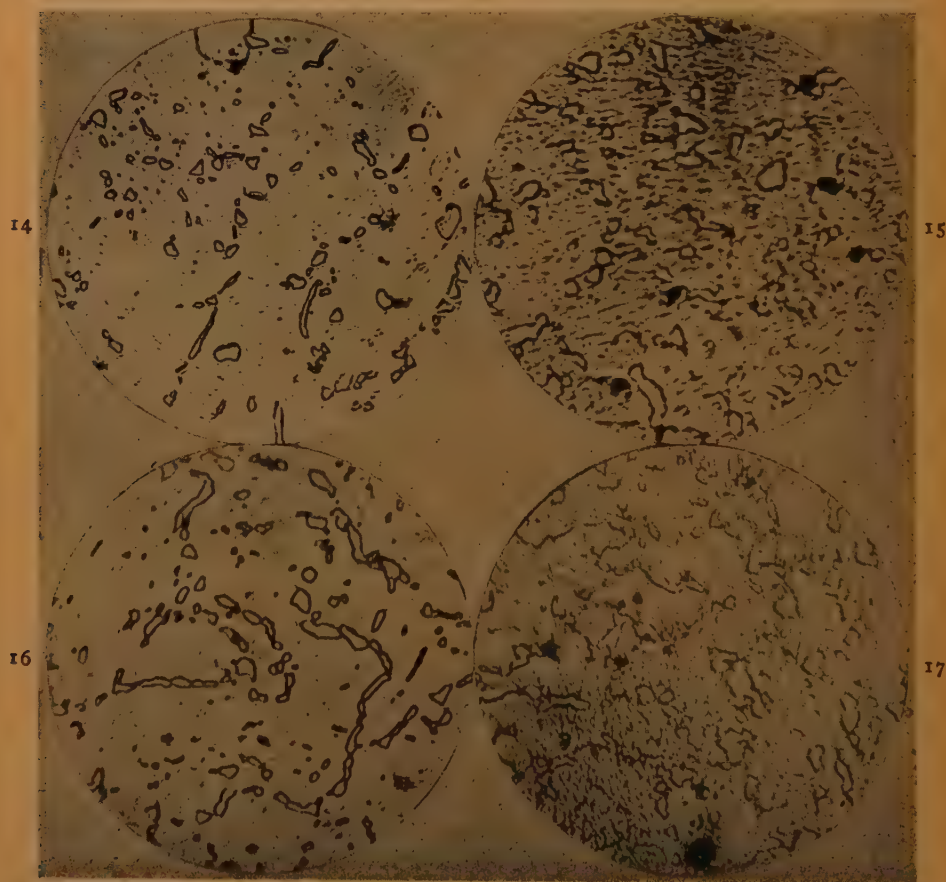
cent C). In the higher carbon range the reduction in area is about one fourth to one tenth of the values for S.A.E. plain carbon steels. This can again be accounted for by the results shown in Table 3. All sintered metals exhibit this low reduction in area, and only by hot-working can the residual porosity be eliminated and figures for reduction in area brought up closer to those for regular metals.

4. The impact values for the sintered steels are extremely low because of the residual porosity. Values for furnace-

cooled and oil-quenched samples are approximately as follows:

C, PER CENT	AV. IZOD IMPACT, FT.-LB.
0.28	9.5
0.52	5
0.64	3
0.87	2

In addition, the hardness values for the sintered steels as measured with a Rockwell machine were found to be low as compared with equivalent S.A.E. steels. This again can be explained by our residual



FIGS. 14-17.—MIXTURES I, II, III AND IV FURNACE-COOLED, REHEATED TO 1525° TO 1575° F., OIL-QUENCHED, TEMPERED AT 1300° F. $\times 1000$. ETCH PICRAL.

Fig. 14. Mixture I; C, 0.28 per cent.

Fig. 15. Mixture II; C, 0.52 per cent.

Fig. 16. Mixture III; C, 0.64 per cent.

Fig. 17. Mixture IV; C, 0.87 per cent.

porosity, which permits the hardened steel ball to penetrate to a greater depth. In addition, the complete absence of such elements as silicon and manganese in the sintered steels makes them much more sluggish in transforming to harder structures on rapid cooling.

Figs. 6 to 9 show porous steels with coarse-lamella pearlite caused by the comparatively slow cooling rate in the non-heated portion of the muffle and the high purity of the steel.

Figs. 10 to 13 reveal a much finer

pearlitic structure with fewer ferrite areas.

Figs. 14 to 17 show a spheroidized cementite structure due to the oil quench followed by a 1300°F. temper. This type of structure has higher elongation and reduction in area with correspondingly lower yield and tensile strengths.

Figs. 18 to 21 show a very fine pearlite with decreasing amounts of ferrite as the carbon content increases. The water quench was not drastic enough to form martensite in the central portion of the



FIGS. 18-21.—MIXTURES I, II, III AND IV FURNACE-COOLED, REHEATED TO 1525°F., WATER-QUENCHED, TEMPERED AT 600°F. $\times 1000$. ETCH PICRAL.

Fig. 18. Mixture I; C, 0.28 per cent.

Fig. 19. Mixture II; C, 0.52 per cent.

Fig. 20. Mixture III; C, 0.64 per cent.

FIG. 21. Mixture IV; C, 0.87 per cent.

test bar, even with the highest carbon content.

REDUCED IRON PLUS GRAPHITE

Raw Materials

Several grades of reduced powder were investigated in combination with graphite.

cent graphite, were made and bars were pressed in the same manner as the electrolytic iron plus graphite. Fig. 22 shows the structure of the reduced iron powder.

Results on Reduced Iron plus Graphite

The physical properties for equivalent carbon contents are far inferior in the reduced powder plus graphite. This is

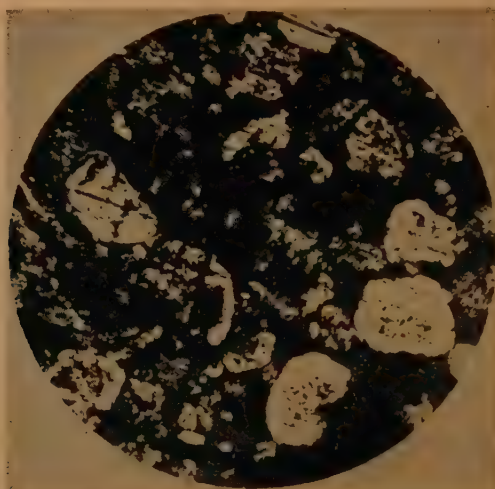


FIG. 22.—REDUCED IRON POWDER AS POLISHED. $\times 75$.

The results on all types investigated were far inferior to those obtained with electrolytic iron plus graphite. The properties of the reduced iron powder that gave the best results were as follows:

Carbon.....	0.24 per cent
H ₂ loss.....	1.29 per cent
Apparent density....	1.99 grams per c.c.
Flow.....	33.1 sec. per 50 grams
	PER CENT

Screen Analysis:

+100.....	1.5
-100 + 140.....	20.5
-140 + 200.....	26.0
-200 + 230.....	6.0
-230 + 325.....	16.0
-325.....	30.0
Total.....	100.0

Mixtures I, II, III and IV, containing respectively 0.40, 0.65, 0.85 and 1.05 per

cent carbon steel are compared for reduced powder plus graphite and electrolytic iron plus graphite. The treatments are specified by means of the following symbols:

P, press at 50 tons per sq. inch.
S, sinter 2000°F. for 15 min. Cracked propane, ratio 80 to 10.
RP, repress at 50 tons per square in.
RS, resinter 2000°F. for 1 hr. Cracked propane, ratio 80 to 10.
A, anneal 1500°F. for 30 min. Cracked propane, ratio 80 to 10.
D, draw
WQ, water quench
OQ, oil quench
 δ , density
HF, hot-forged after *P*, *S*, *RP*, *RS*. This was done by 10 reheatings and forgings in the temperature range 2000° to 1600°F. The bar was forged to 50 per cent reduction in area. After forging, the bar was normalized at 1600°F.

By comparing Figs. 25 to 28 with Figs. 6 to 9, some understanding of the causes of inferior properties in the bars made from reduced iron plus graphite can be

3. Large pores and oxide inclusions are present in the steel made from the reduced powder. This again is a characteristic of reduced powder even when

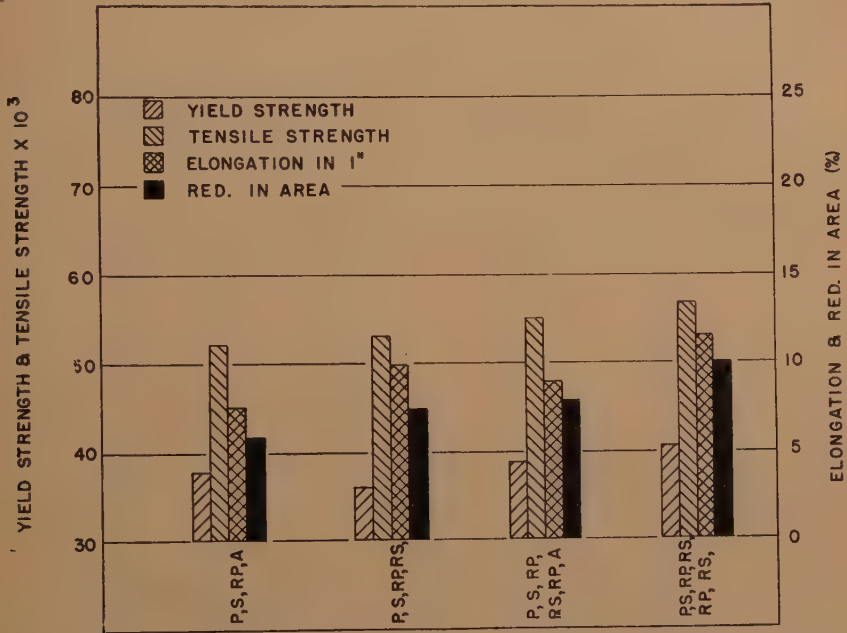


FIG. 23.—PHYSICAL PROPERTIES VS. TREATMENT, REDUCED IRON POWDER PLUS GRAPHITE.

obtained. The differences in microstructure to be noted are:

1. The final carbon content of the mixtures of reduced powders is in all cases lower than that of the mixtures of electrolytic powder, because of the higher hydrogen loss for the reduced powder.

2. The pearlite is not uniformly distributed in the reduced powder. This is because the oxide content of reduced powder is not limited to the surface of the power particles but also occurs inside the particles, in a random and unpredictable manner. Thus in some areas the graphite might be used up entirely in reacting with oxide inclusions and in other areas some graphite might be left over after reacting with oxide inclusions and surface-absorbed oxygen to diffuse into the iron.

straight iron parts are pressed and sintered. In addition, the spongy particles of reduced powder have a tendency to spring back after deformation or to resist plastic deformation. This accounts for the lower density of bars made from the reduced powder, and the lower density plus the large number of large pores and oxide inclusions scattered through them at random account for the poorer physical properties of the mixtures of reduced powder and graphite.

CONCLUSIONS

Sintered steels can be made easily by the method outlined in this report. If made from electrolytic iron plus graphite these steels will have yield strengths and tensile strengths fairly close to those of

S.A.E. plain carbon steels, but will be considerably lower in elongation, reduction in area and impact strength. The residual porosity is responsible for the low ductility and poor impact strength.

The microstructure of sintered steels made from electrolytic iron plus graphite and having a final carbon content ranging from 0.28 to 0.87 per cent C differs from S.A.E. plain carbon steels, because the

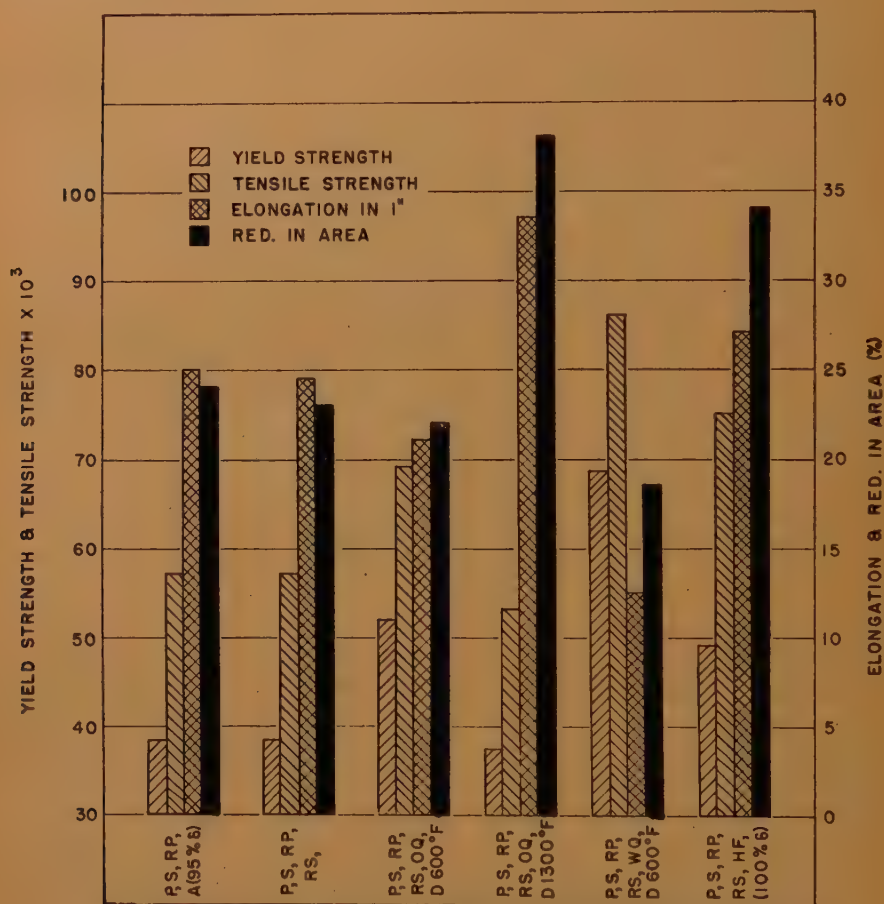
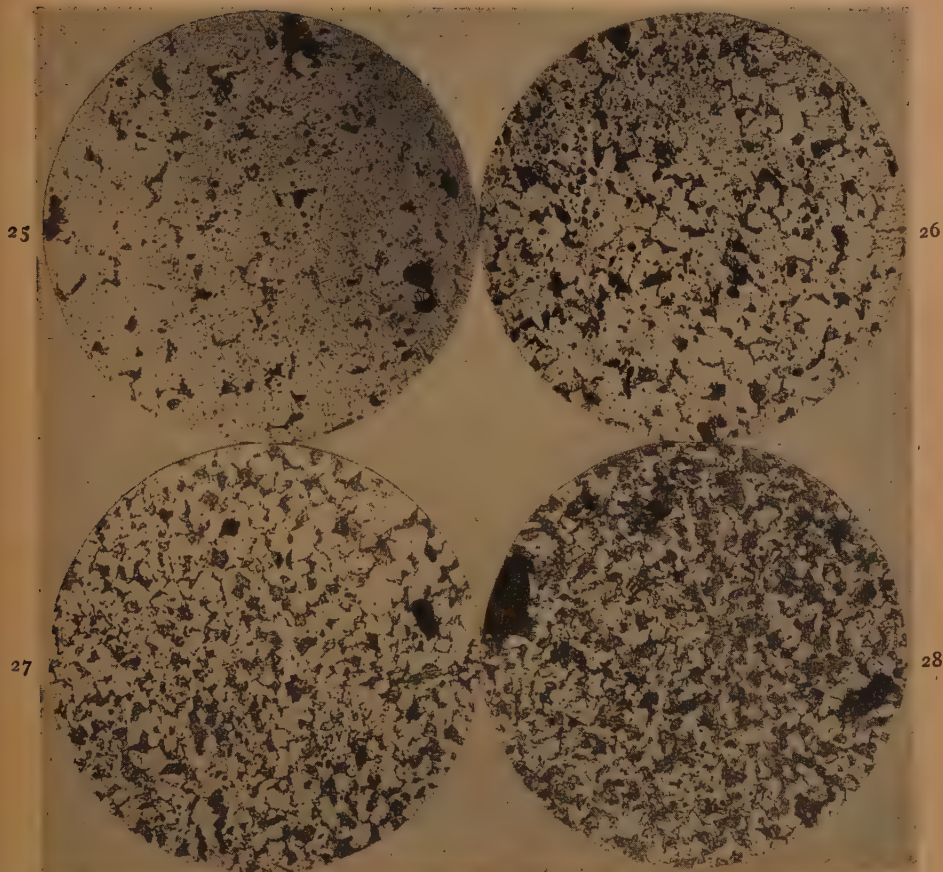


FIG. 24.—PHYSICAL PROPERTIES VS. TREATMENT, ELECTROLYTIC IRON AND GRAPHITE.

These sintered steels can be heat-treated in exactly the same way as S.A.E. plain carbon steels, but greater care must be taken to have a neutral and dry atmosphere owing to the porosity and greater surface exposed to the action of the atmosphere. By heat-treatment the properties can be varied in much the same way as with ordinary steels.

sintered steels do not transform to a martensitic structure when oil-quenched or water-quenched in the $\frac{5}{8}$ by $\frac{5}{8}$ -in. cross section studied. Other differences in microstructure are the greater porosity and a slight tendency toward abnormality in the samples slowly cooled from the sintering temperature. This abnormality is in the form of coarse pearlite with an



FIGS. 25-28.—TEST BARS, PRESSED, SINTERED, REPRESSED AND RESINTERED, REDUCED IRON AND GRAPHITE. $\times 200$. ETCH PICRAL.

Fig. 25. Mixture I; C, 0.14 per cent.

Fig. 26. Mixture II; C, 0.27 per cent.

Fig. 27. Mixture III; C, 0.36 per cent.

Fig. 28. Mixture IV; C, 0.58 per cent.

occasional isolated individual lamella due to the high purity of the steel.

The physical properties of compacts made from reduced iron plus graphite are below those of mixtures of electrolytic iron and graphite, similarly treated, when compared on the basis of final carbon contents. An explanation for the superior properties on electrolytic iron plus graphite over reduced iron plus graphite is given on the basis of density values and microstructure.

ACKNOWLEDGMENT

The author wishes to express his appreciation to Dr. Paul Schwarzkopf, Director of Research, American Electro Metal Corporation, Yonkers, N.Y., for his guidance and encouragement in this investigation. The assistance of Mr. Joseph P. Scanlan in the performance of the experimental work is also gratefully acknowledged.

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DISCUSSION

(R. P. Seelig presiding)

W. T. SNYDER.*—The author talks about carbon contents, and although he added graphite, I should like to know whether he is talking about combined carbon or total carbon. A second question is: in his heat-treated samples, those that he quenched both in water and in oil, he shows structures that are definitely pearlitic. I should like to know in what size sections he quenched them, because it is well known that in pure iron-carbon alloys in very thin sections or small sections, either a martensitic or a bainitic structure is obtained.

GEORGE STERN (author's reply).—Graphite was added to our iron powders in making up the mixtures, but after our processing cycle—consisting of a pressing, a presintering, a repressing, and a final sinter at 2000°F.—all the carbon was definitely combined.

In answer to the second question: the bars were 3 in. long and $\frac{5}{8}$ by $\frac{5}{8}$ in. in cross section. The bars were heat-treated in this size and, apparently owing to the high purity of our steels, pearlite was formed in the center of the cross section. Of course, the tensile bar had a 0.250-in. diameter, which represents the center portion of the $\frac{5}{8}$ by $\frac{5}{8}$ -in. cross section.

JOHN WULFF.†—The author of this paper is

* Powdered Metal Products, Chicago, Illinois.

† Professor of Metallurgy, Massachusetts Institute of Technology, Cambridge, Massachusetts.

to be congratulated on the excellent experimental data presented. In his work, the powders made from reduced oxide do not give comparable results. Might not the results be just as good with reduced powders as with electrolytic powders if the sintering cycle were changed? Specifically, would not a longer heating time at low temperatures ensure total reduction of residual oxides and elimination of deleterious gases before excessive shrinkage took place?

GEORGE STERN.—Professor Wulff's suggestion is worth while, and should definitely be tried.

It was in no sense intended to imply that reduced powders could not be used for high-strength parts. As a matter of fact, we have developed high-strength parts using reduced powder. I cannot go into great lengths as to the method used, but it consists of alloying with small percentages of copper and other elements. We have been very successful in raising the physical properties of steels made from reduced powders by this method, and although residual porosity is still there, causing somewhat lowered values for elongation and reduction in area, our yield and tensile strength go up considerably with the addition of copper and several other elements.

F. H. CLARK.*—As I understand from the paper, the atmosphere used was entirely a lithium atmosphere, was it not?

GEORGE STERN.—It was a modification.

F. H. CLARK.—Did you find any decarburization on the surface in this modified lithium atmosphere? Cracked ammonia atmospheres have been found very satisfactory for sintering iron and graphite mixtures. The author's claim that the specimens had low strength and low impact values might be due to porosity, but there is also the possibility that free carbon was present. Were any chemical tests made to determine whether there was free carbon in the specimens?

GEORGE STERN.—It was necessary for us to make several modifications in the standard type of furnace in order to achieve satisfactory results with a lithium atmosphere. The

* Metallurgist, Western Union Telegraph Co., New York, N. Y.

results reported were obtained by placing lithium salts on the boats carrying the charge as well as in the lithium generator. Table 1 shows how the ratio of air to propane that was considered neutral was obtained experimentally.

In regard to cracked ammonia, it has been found that this atmosphere has an exceptionally low dewpoint, and is therefore ideal in a closed system. However, in our experiments, we tried to use a production furnace that employed opening and closing doors in order to charge and discharge the boats. This procedure raised the dewpoint of the atmosphere in our furnace, resulting in excessive decarburization. We could, of course, get away from this decarburizing effect of the cracked ammonia when the dewpoint was raised, by surrounding the samples with a graphite shell. This graphite shell should not actually be in contact with the samples, but gives the desired result of no decarburization.

The poor impact and elongation obtained in the high-carbon series could not be attributed to free or uncombined graphite, because our sintered samples had no free graphite. The density figures shown in Table 3 are a much more logical explanation for the lowered impact, reduction in area, and elongation values obtained with the higher carbon series (mixtures III and IV). Our porosity increased from 3.8 to 6.1 per cent as our carbon content increased; that is, after presintering, our higher carbon materials tend to resist plastic deformation more, resulting in lower density (higher porosity).

A. SQUIRE.*—What was the particle size of the graphite, and how did you go about mixing the graphite with the iron, to be sure there was a uniform distribution throughout? Was uniformity of structure obtained in the steel specimen?

GEORGE STERN.—The graphite used was all —325-mesh material, but I do not know the exact particle size. The graphite was mixed with the iron powder by tumbling end over end in glass jars for one hour. This was followed by a careful hand-mixing on glazed paper. The pearlite was very uniformly distributed in the steels made from electrolytic iron. This indicates that the graphite was uniformly distributed

throughout the powder mixture. While it is true that the pearlite was not uniformly distributed in the steels made from reduced powder, this has been explained on the basis of random oxide location in the reduced powder, rather than on poor graphite mixing.

A. SQUIRE.—After you had repressed and repressed and resintered, was not the density of the bars less than the density of the electrolytic bars?

GEORGE STERN.—In all cases far below.

A. SQUIRE.—In those cases, the lower tensile and lower ductility are attributable to a great extent to the lower density?

GEORGE STERN.—Yes, I believe that is the explanation.

F. P. PETERS.*—I want to make a brief comment about the possible presence or absence of graphite. The puzzling lamellar pearlitic structure that you obtained after quenching indicates a material of lower hardenability than would be expected. This lowered hardenability could be the result of graphite formation, leaving insufficient combined carbon to produce a fully martensitic steel on quenching. On the other hand (carbon having less effect on hardenability than do the conventional steel-alloying elements) the thickness of your samples may simply have been too great to harden throughout even if all the carbon was in the combined form. I wonder if there is anyone in the audience who knows offhand what the depth hardenability would be of steel specimens of the size that Mr. Stern quenched and of the carbon content he presumes he had in the combined form?

F. V. LENEL.†—I would like to insert one thing in that connection. Did you heat-treat the material after it was machined or before it was machined?

GEORGE STERN.—Before it was machined, so that the section was actually $\frac{5}{8}$ by $\frac{5}{8}$ in. The bars were used for making tensile bars and micrographs were taken of the $\frac{1}{4}$ -in. diameter reduced section.

* *Materials and Methods*, New York, N. Y.

† Moraine Products Division, General Motors, Dayton, Ohio.

* Westinghouse Electric Corporation, Pittsburgh, Pennsylvania.

AARON FINGER.*—On an extensive series of alloys similar to these prepared with the 8485 graphite, we ran chemical analyses and found that in 50 min. at 1100°C. there was no longer any uncombined carbon present. We went up in steps of 10 min., 15 min., 20 min., 30 min., 40 min., all the way up, and conclusively, for our purpose, came to the findings that after 50 min. all carbon had combined.

On other grades of graphite—finer grades—we found that complete combination took place in as little as 15 min. A procedure similar to that followed in this paper probably would not show up so well because we get the combination during presintering, thereby making the compact difficult to repress. Using the finer materials, however, we got the values in the order of 75,000 lb. per sq. in. by pressing once and sintering, which correspond to the values reported by Mr. Stern.

I want to ask a question on elongation, because that is something we discussed at length. First of all, how did you measure the elongation?

GEORGE STERN.—Thank you, Mr. Finger, for supplying this very interesting information. In our experiments, we had a presintering time of 15 min. at 2000°F. plus a second sintering at 2000°F. of 60 min.; thus making a total of 75 min. at 2000°F. Therefore, I think it is pretty definitely established on the basis of Mr. Finger's observations that we had no free graphite in our final samples.

As far as the elongation is concerned, we machined a tensile bar from our $\frac{5}{8}$ by $\frac{5}{8}$ by 3-in. bar. This tensile bar had a diameter of 0.250 in. and a gauge length of 1 in. By means of a punch, we had two points exactly one inch apart on our gauge length. The elongation was measured by fitting the ruptured bar together and inserting dividers in the two punch marks.

AARON FINGER.—I found the figures startling. They are three to four times as high as we have found.

GEORGE STERN.—Do you use a machined bar for your tensile specimens?

AARON FINGER.—We use a flat tensile specimen.

GEORGE STERN.—There is a great deal of controversy as to the relative merits of a machined tensile bar and a flat pressed tensile bar in the field of powder metallurgy. It is quite possible that if a flat pressed bar is water-quenched and drawn, it would no longer be straight. This could easily result in lower elongation values in the pulling of such a bar. It is my opinion that it is easier to heat-treat a more rigid bar, such as the one we used, and then machine it to form a tensile bar. However, I think it is up to the American Society for Testing Materials to decide on the type of tensile bar to be used. I would like to see both adopted.

C. G. GOETZEL.*—I would like to comment briefly on the elongation. Apparently the type of iron powder used has some effect on the compact's ductility. Not every electrolytic iron powder acts in the same way, and some give better elongation values after sintering than others. We experimented with one type of electrolytic iron powder that very recently made an appearance on the market, and that gave us better tensile strengths and elongations than had been previously experienced with other electrolytic powders; so I feel one should consider the type of iron powder as well as graphite in judging the test results.

F. V. LENEL.—I should like to emphasize somewhat more what Mr. Snyder said about the analysis of this material. Mr. Stern called the material steel, and of course, there is a similarity between the analyses of the alloys he made and SAE steel, but there is also a dissimilarity, and a very important one, inasmuch as all SAE steels contain a considerable amount of manganese. If I remember rightly, most of the steels that Mr. Stern used for comparison purposes contained between 0.6 and 0.9 per cent manganese. A material containing such an amount of manganese will have a much higher hardenability than a material that does not contain any manganese at all. The effect of hardenability will be found not only in the hardness Mr. Stern referred to, but also in the microstructure and in the strength values.

I feel that the lower strengths of the higher carbon materials, the 60 and 80 carbon materials might be due to the difference in

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*Electro Metals Corporation, Yonkers, New York.

TABLE 4.—*Comparison of Brinell Hardness Values of SAE and Sintered Steels*

Treatment	1030		1045		1060		1080	
	SAE	Sin.	SAE	Sin.	SAE	Sin.	SAE	Sin.
Furnace cooled.....		124		137		132		158
Oil-quenched, drawn 1300°F.....	170	120	196	126	201	132	217	135
Oil-quenched, drawn 600°-800°F.....	223	134	277	146	293	161	363	177
Water-quenched, drawn 600°F.....	241	158	311	203		218		245

hardenability between the synthetic materials and SAE steels rather than to any other effect.

GEORGE STERN.—I thank Mr. Lenel for calling attention to this fact. The absence of manganese and other elements that might contribute to hardenability was mentioned in the paper, but perhaps it was not sufficiently emphasized in my oral presentation. For example, in the electrolytic iron, we have no manganese or silicon, both of which are present in SAE steels. I think that is a very important point.

MEMBER.—I fail to remember any mention of hardnesses. Did you include that in your paper?

GEORGE STERN.—Hardness values were actually taken, but are not given quantitatively in the paper.

MEMBER.—In what order were they punched?

GEORGE STERN.—I believe that the data in Table 4 will answer that question.

Nickel-iron Alloys Produced by Powder Metallurgy

BY LAURENCE DELISLE* AND AARON FINGER†

(Chicago Meeting, February 1946.)

THE alloys formed by the addition of nickel to iron by conventional metallurgical procedures show physical properties that differ widely from those of the individual metals. The effect of alloying on the mechanical properties is most pronounced in alloys containing between 15 and 25 per cent nickel. The tensile strength of an alloy containing, for example, 20 per cent nickel and 80 per cent iron (with 0.06 per cent carbon), in an annealed condition, is above 150,000 lb. per sq. in.‡ owing to a martensitic type of transformation, as compared with about 50,000 lb. per sq. in. for pure iron in the same condition. The object of this work was to determine whether the same beneficial alloying effect could be obtained in alloys of iron and nickel prepared by powder metallurgy technique.

PROCEDURE

Bars and pellets for tension and compression tests, respectively, were made. Two groups of specimens were prepared: (1) by cold-pressing the powders and sintering; (2) by cold-pressing the powders, sintering, repressing and resintering.

Raw Materials

Nickel powder supplied by Metals Disintegrating Co., marked MD-151, was

Manuscript received at the office of the Institute Jan. 25, 1946. Issued as T.P. 2046 in METALS TECHNOLOGY, August 1946.

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† Research Fellow, Department of Powder Metallurgy, Stevens Institute of Technology.

‡ Value given by Pilling and Brophy: Alloys of Iron and Nickel, 1. Alloys of Iron Monographs. New York, 1938. McGraw-Hill Book Co.

used. A typical analysis of this powder was as follows: sulphur, 0.040 per cent; copper, 0.18; iron, 0.23; manganese, 0.002; magnesium, 0.0015; lead, 0.035; tin, 0.025; silicon, 0.08; chromium, 0.008.

Electrolytic iron powder supplied by Plastic Metals Inc. was used. A representative chemical analysis for impurities other than gases, supplied by the vendor, gave the following results: carbon, 0.005 per cent; manganese, 0.002; silicon, 0.003; phosphorus, 0.001; sulphur, 0.004; nickel, 0.008.

The fractions from these powders passing a 325-mesh sieve were reduced in hydrogen at 600°C. for one hour, to clean the surfaces of the particles. The reduced powders, slightly caked, were ground in a mortar and screened again through a 325-mesh sieve.

Mixing

The proper proportions of the powders were mixed overnight on rolls, in glass jars fitted with iron-wire baffles to break aggregates of particles that might form.

Pressing

All specimens were compacted on hydraulic presses. The pellets were compacted in a cylindrical die, ½-in. diameter. The ratio of thickness to the diameter of the pellets was maintained as nearly as possible at 0.9, as specified for standard short compression pieces. The tensile bars were made by compacting 30 grams of powder. Their shape is shown in Fig. 1.

The compacting pressures for the pellets and the tensile bars were:

	TONS PER SQ. IN.
For specimens pressed only once	50
First compacting of specimens to be repressed.....	30
Second compacting of speci- mens already pressed (30 tons per sq. in.) and presintered..	75

Sintering

All sintering was done in hydrogen that was first passed over heated copper coils, then through an activated alumina tower

Sintering was carried out in a tubular electric furnace. The specimens were heated with the furnace, kept at the sintering temperature for the specified time, and brought out of the hot zone slowly. Cooling to room temperature required 2 hours.

Testing

Compression.—The compression was applied to pellets about 0.50 in. in diameter

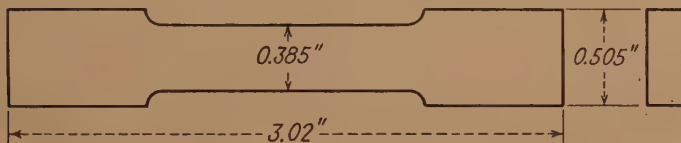


FIG. 1.—SHAPE OF TENSILE BARS.

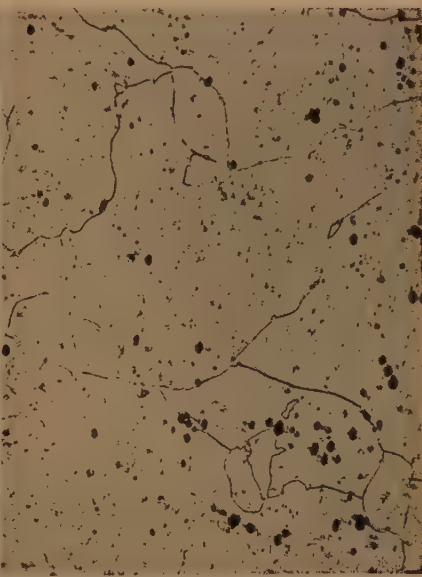


FIG. 2.—100 PER CENT NICKEL POWDER, REPRESSED. $\times 200$. ETCHANT, MERICA'S REAGENT.
FIG. 3.—100 PER CENT IRON POWDER, REPRESSED. $\times 200$. ETCHANT, 1 PER CENT NITAL.

and finally a P_2O_5 tower for the removal of oxygen and water.

Specimens pressed only once were sintered for 3 hr. at 1100°C . Specimens pressed and sintered twice were sintered first $\frac{1}{2}$ hr. at 1100°C . and resintered, after repressing, at the same temperature for 3 hours.

and 0.45 in. thick. The total load applied varied from 2000 to 20,000 lb. in increments of 1000 lb. After each application of load, the pressure was released and the thickness at the center of the specimen was measured with a micrometer.

Tension.—The bars were pulled on a mechanical tensile machine and their

ultimate strength and elongation were recorded. Often the bars broke nearer a fillet than the center of their reduced section. Under such conditions it is difficult to obtain a true value for the elongation. However, the figures given in Table 1 show the relative approximate ductility of the alloys studied.

RESULTS

The results are given in Table 1 and shown in the micrographs and graphs of Figs. 2 to 21.

TABLE 1.—*Mechanical Properties of Nickel-iron Alloys^a*

Per- centage of Nickel	Den- sity, Grams per C. C.	Rock- well B Hard- ness	Ulti- mate Tensile Strength, Lb. per Sq. In.	Elonga- tion, Per Cent in 1.5 In.	Yield Strength in Compression, Lb. per Sq. In.	
					0.2 Per Cent Off- set	1.0 Per Cent Off- set
Bars Pressed and Sintered Once						
0	7.14	6	33,700	25.7	1,000	6,000
10	7.37	74	60,100	9.6	9,000	52,000
15	7.24	81	71,700	2.3	55,000	70,000
20	7.36	85	84,100	4.0	42,000	66,000
25	7.46	85	73,500	4.7	35,000	62,000
30	7.44	71	56,600	5.1	20,000	46,000
40	7.50	57	57,600	9.7	8,000	30,000
50	7.45	54	47,800	10.4	13,000	26,000
60	7.53	62	62,500	10.3	14,000	27,000
70	7.66	65	46,500	7.4	16,000	27,000
80	7.68	53	45,800	6.7	12,000	21,000
90	7.96	49	32,100	...	8,000	17,000
100	8.25	24	32,900	10.1	1,000	6,000
Bars Pressed and Sintered Twice						
0	7.66	19	39,200	48.0	11,000	14,000
10	7.55	79	69,300	15.8	27,000	55,000
15	7.33	86	81,000	1.3	42,000	70,000
20	7.48	93	106,700	4.4	52,000	85,000
25	7.52	89	84,000	4.4	47,000	70,000
30	7.63	76	68,500	10.3	36,000	57,000
40	7.61	62	61,000	11.7	23,000	35,000
50	7.76	66	66,200	25.3	17,000	31,000
60	7.82	72	69,100	14.0	26,000	35,000
70	7.99	73	60,300	14.1	29,000	35,000
80	8.16	70	43,900	5.3	25,000	30,000
90	8.32	62	58,100	21.5	10,000	23,000
100	8.60	34	47,500	26.7	3,000	12,000

^a The deformation in compression was recorded as described under testing. The values given in this table were interpolated. The low values may be considerably in error. However, the differences in the values due to composition are so striking and so large in comparison with the possible error in calculation that it seemed worth while to report them. The yield-strength values generally follow the trend exhibited by those for tensile strength in Fig. 19.

Microscopic Examination

Specimens pressed and sintered once are more porous than the specimens pressed and sintered twice and the porosity is more uniformly distributed in the latter than in the former.

All micrographs illustrate the structure of samples pressed and sintered twice. Figs. 3, 4, 5, 6 and 7 (magnification: 200 diameters) show the effect of etching one minute with 1 per cent nital. The grain size of the specimens containing nickel is much smaller than that of the samples made of pure iron. The amount of iron-rich constituent attacked by 1 per cent nital in one minute decreases as the nickel content increases, until when that content reaches 70 per cent no etching at all is obtained. The iron-rich constituent seems to form a continuous pattern in the specimens containing 10 per cent nickel. Such a continuity is broken when 20 per cent nickel is present. Figs. 8, 9 and 10 show the structure, at a magnification of 500 diameters, of the specimens containing respectively 15, 20 and 25 per cent nickel, also etched one minute with 1 per cent nital. Some grains have an acicular structure.

Merica's reagent (glacial acetic acid + concentrated HNO_3) attacked the specimen made of pure nickel readily (Fig. 2), but it had no effect on the nickel-rich samples nor on the nickel-rich constituents of the iron-rich samples. Grard's reagent did not give any better results. A reagent containing 25 c.c. HNO_3 , 25 c.c. HCl and 25 c.c. H_2O produced a satisfactory etching of the specimen containing 70 per cent nickel by flooding for 3 min. (Fig. 11). The time of etching had to be increased for the specimen containing 90 per cent nickel (Fig. 12). The same reagent was applied, after the 1 per cent nital etch, to the specimens containing 15 and 20 per cent nickel. In that case, better results were obtained by swabbing (Fig. 13 and 14). The specimens containing 70 and 90 per cent nickel have a rather homo-

geneous structure; the specimens poorer in nickel are heterogeneous. In Fig. 13 (15 per cent nickel), the nickel-rich core is clearly visible. Its grains have an irregular boundary and are surrounded by an un-

have an angular boundary. The grains of the other constituents are much more irregular.

Figs. 15 and 16 are photographs of the powders used.



FIG. 4.—10 PER CENT NICKEL, 90 PER CENT IRON.
 FIG. 5.—20 PER CENT NICKEL, 80 PER CENT IRON.
 FIG. 6.—30 PER CENT NICKEL, 70 PER CENT IRON.
 FIG. 7.—50 PER CENT NICKEL, 50 PER CENT IRON.
 X 200. ETCHANT, 1 PER CENT NITAL.

etched zone, which stains easily. The specimen shown in Fig. 14 (20 per cent nickel) was attacked more readily. The nickel-rich core is smaller and its few grains

DISCUSSION OF RESULTS

Density (Figs. 17 and 18)

The general trend is an increase in density with the nickel content, before

and after sintering. However, the change is not linear and, in some cases, a specimen richer in nickel is less dense than one poorer in nickel treated in the same way.

The density increases for all compositions when the compacting pressure is increased from 30 to 50 tons per sq. in. For all compositions, it also increases on

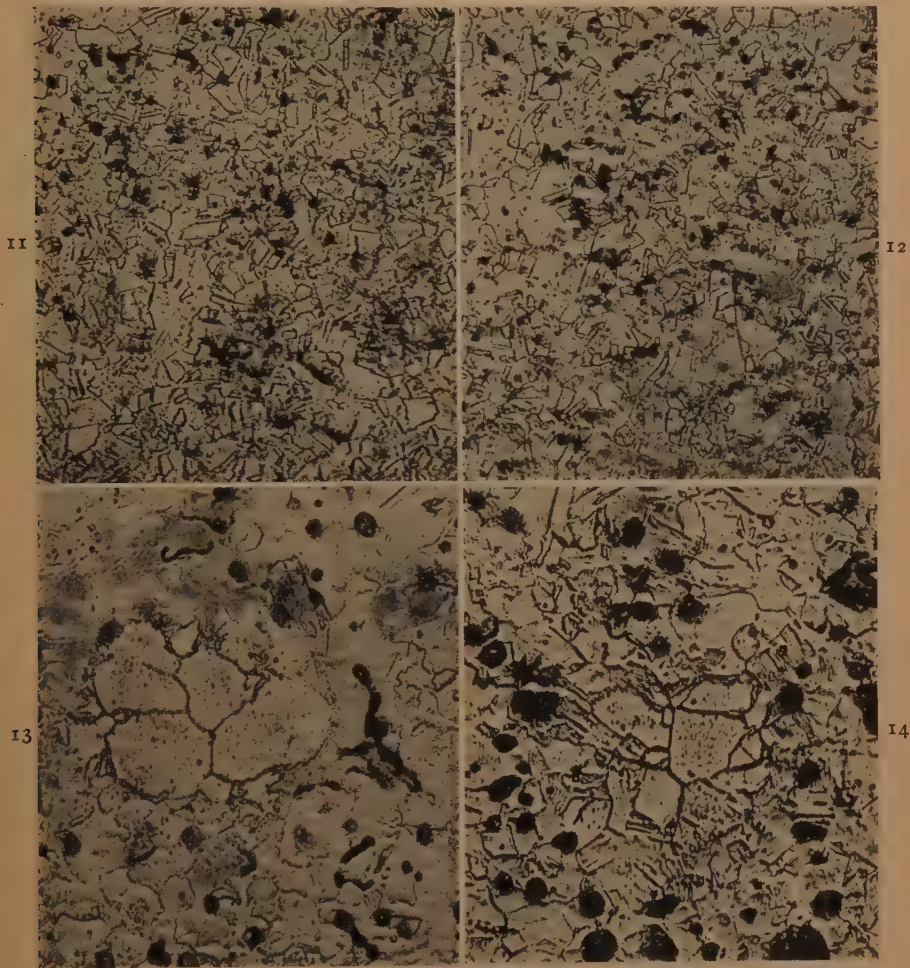


FIG. 11.—70 PER CENT NICKEL, 30 PER CENT IRON.
 FIG. 12.—90 PER CENT NICKEL, 10 PER CENT IRON.
 × 200. ETCHANT, 25 c.c. HNO_3 , 25 c.c. HCl , 25 c.c. H_2O .
 FIG. 13.—15 PER CENT NICKEL, 85 PER CENT IRON.
 FIG. 14.—20 PER CENT NICKEL, 80 PER CENT IRON.
 × 500. ETCHANT, 25 c.c. HNO_3 + 25 c.c. HCl + 25 c.c. H_2O .

It is noticeable, for instance, that specimens containing 10 per cent nickel, pressed and sintered twice, are not as dense as specimens made of pure iron under the same conditions.

sintering as well as on repressing and resintering.

The same general trend in the relation of the density to composition is observed with the pellets as with the tensile bars.

In the former, however, the values seem more erratic. This difference in the behavior of the two types of specimens may be due to the difference in their thickness. The

20 per cent nickel, pressed and sintered twice, attains 106,700 lb. per sq. in. as compared with 39,200 and 47,500 lb. per sq. in. for the bars made of pure iron and



15



16

FIG. 15.—IRON POWDER, 100-MESH FRACTION. $\times 200$. ETCHANT, 1 PER CENT NITAL.

FIG. 16.—NICKEL POWDER, 325-MESH FRACTION. $\times 200$. ETCHANT, MERICA'S REAGENT.

pellets are much thicker than the tensile bars and the effect of the slight flow of powders in compacting is probably more appreciable in these thicker specimens. A lower degree of uniformity in the distribution of the pressure may be expected to cause a corresponding lack of uniformity in the results.

Tensile Strength (Fig. 19)

There is a sharp increase in tensile strength as the nickel content is increased from 0 to 20 per cent, followed by a sharp decrease to 30 per cent nickel. The tensile strength of the alloys richer in nickel varies to a lesser degree with the composition.

The peak value for the tensile strength as the nickel content reaches 20 per cent is observed in both groups of specimens, in those pressed and sintered once as well as in those pressed and sintered twice. The tensile strength of the bars containing

pure nickel, respectively, under the same conditions. The tensile strength of the bars of the same composition pressed and sintered only once is 84,100 lb. per sq. in., which compares with 33,700 and 32,900 lb. per sq. in., respectively, for the specimens made of pure iron and pure nickel.

Repressing and resintering generally increase the tensile strength.

Yield Strength (Fig. 19)

The effect of the nickel on the yield strength of the alloys in compression is similar to its effect on the tensile strength. A peak is observed also in the composition range 15 to 20 per cent nickel. Further additions of nickel cause a sharp decrease in the yield strength to 40 per cent nickel. The effect of the addition of nickel is much less pronounced in the alloys richer in that metal.

Hardness (Fig. 19)

The curves showing the relation of the hardness to the composition follow the same trend as those relating the tensile

Elongation (Fig. 19)

Generally the relation of the elongation to the composition is the reverse of that of the tensile strength, the yield strength

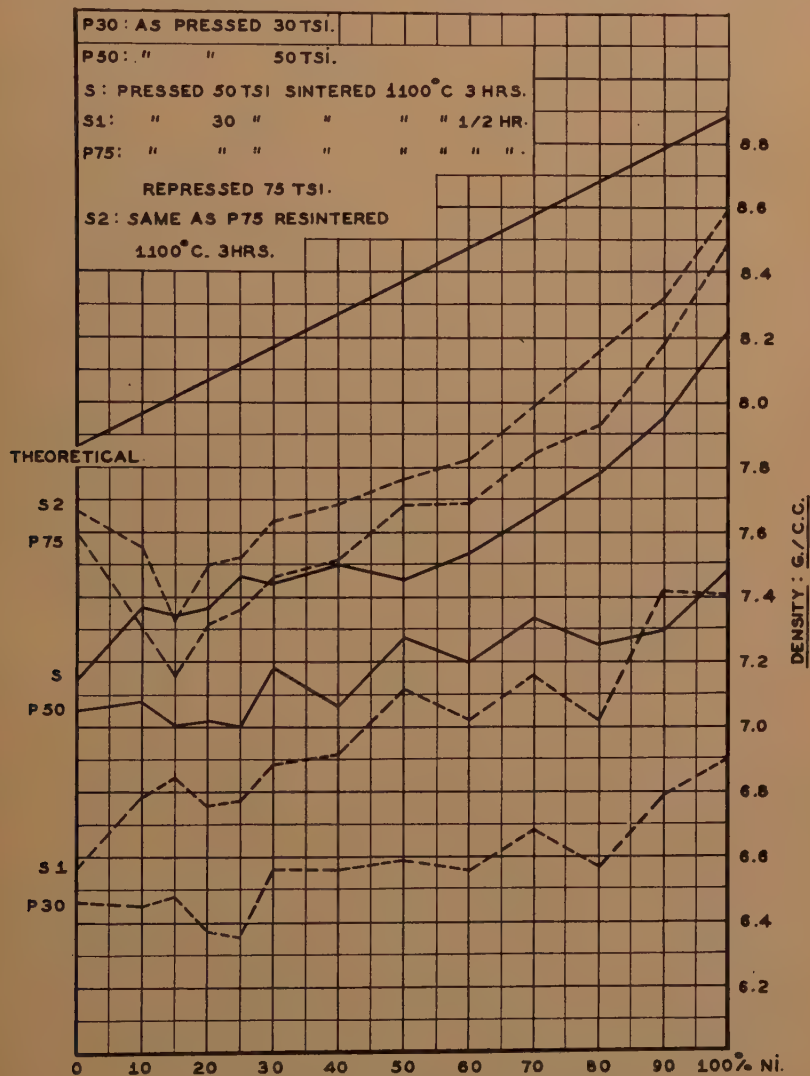


FIG. 17.—DENSITY AND COMPOSITION, TENSILE BARS.

and yield strengths to the composition. A maximum is observed also at a nickel content of 20 per cent. The specimens pressed and sintered twice are harder than those pressed and sintered only once.

and the hardness. The elongation of the specimens pressed and sintered twice is the same as or greater than that of the bars pressed and sintered once.

Microstructure

Alloys containing 50 per cent nickel or less are heterogeneous after the treat-

attacked under the same conditions. As the nickel content is increased the amount of iron-rich constituent etched by 1 per

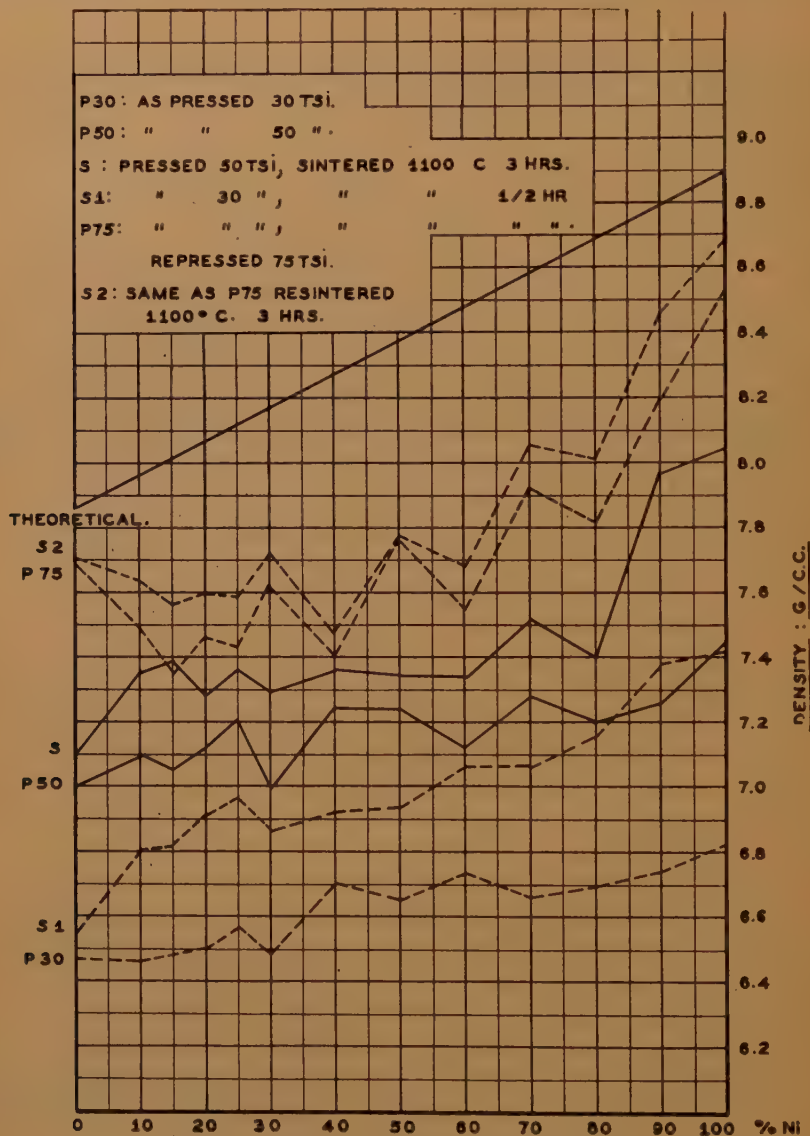


FIG. 18.—DENSITY AND COMPOSITION, PELLETS.

ments employed. They show an iron-rich constituent that is etched in one minute with 1 per cent nital as well as a nickel-rich constituent that remains un-

cent nital in one minute decreases (Figs. 4 to 7); specimens containing more than 50 per cent nickel are not etched at all in that manner. Specimens containing

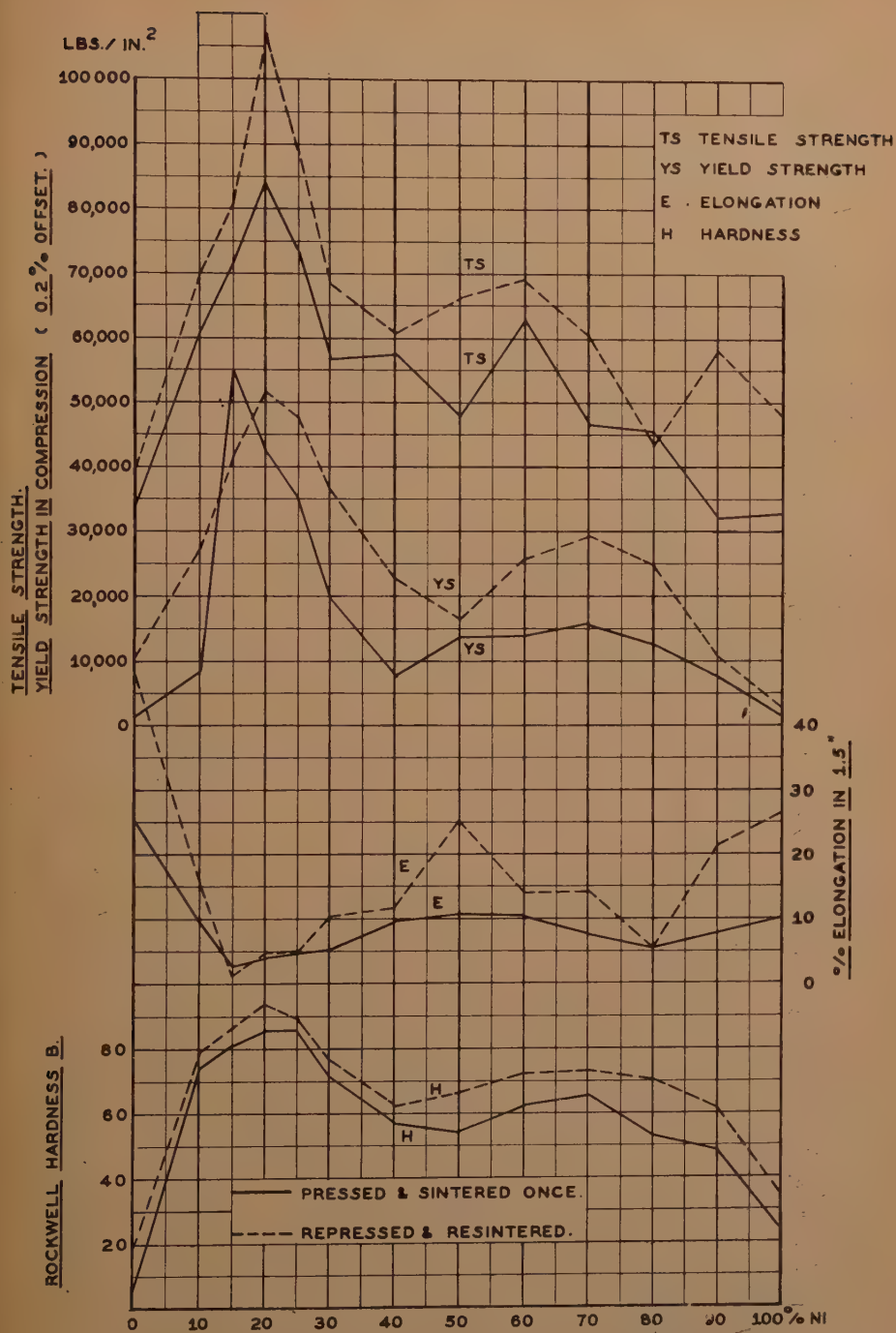


FIG. 10.—TENSILE PROPERTIES AND HARDNESS VS. COMPOSITION.

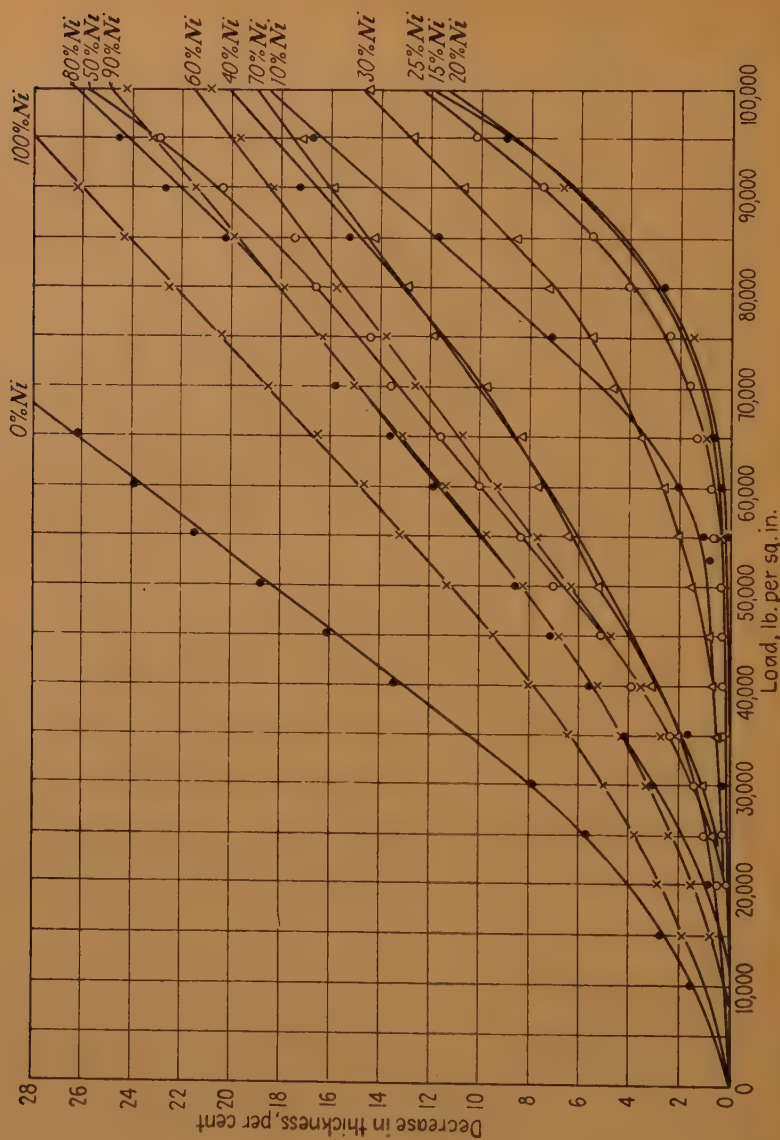


FIG. 20.—COMPRESSION TEST. PERCENTAGE OF SET AFTER VARIOUS LOADS. SPECIMENS PRESSED AND SINTERED ONCE.

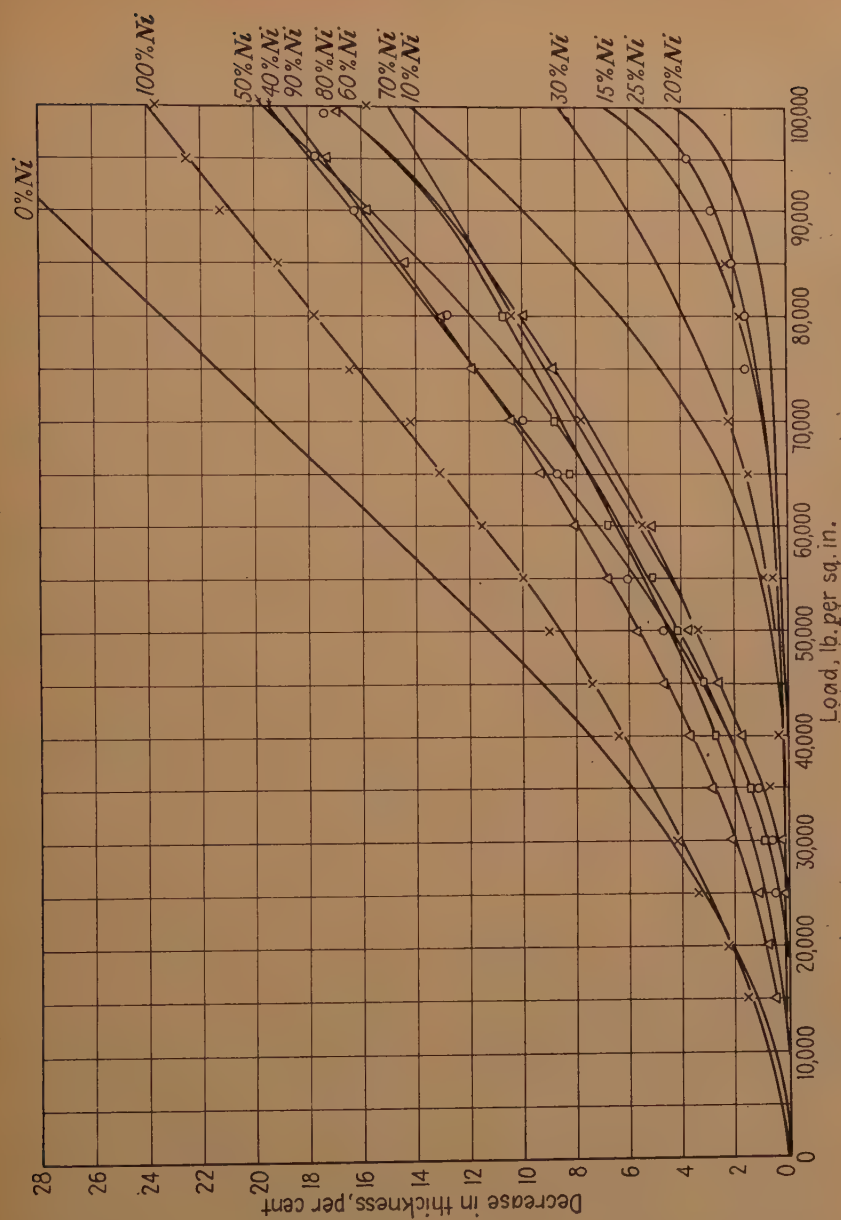


FIG. 21.—COMPRESSION TEST. PERCENTAGE OF SET AFTER VARIOUS LOADS. SPECIMENS PRESSED AND SINTERED TWICE.

70 and 90 per cent nickel require a strong reagent for etching (an aqueous solution of HCl and HNO_3). They are practically homogeneous (Figs. 11 and 12). These high-nickel alloys, as well as the nickel-rich cores of the specimens rich in iron, remained unattacked by a mixture of glacial acetic acid and nitric acid under conditions that produced etching of the pure nickel specimens.

A solution of nitric and hydrochloric acid had also to be used to etch completely the alloys containing 20 per cent nickel. The alloy containing 15 per cent nickel was not etched completely (Figs. 13 and 14). Both alloys stain readily, especially the one containing 15 per cent nickel. The presence of martensitic type transformation products and the heterogeneity of the specimens are probably responsible for this uneven etching.

CONCLUSIONS

This work shows that with both constituents in the solid state diffusion has proceeded to a large extent. This statement is proved by: (1) the physical properties, which are not intermediate between those of pure iron and pure nickel but follow the same general trend as those of the alloys made conventionally, and show critical values in the range 15-20 per cent nickel; (2) the microstructure, which shows that no pure iron is left in the specimens containing 70 and 90 per cent nickel and that the amount of that metal in the specimens poorer in nickel is much less than would be present had no diffusion taken place.

It is evident that essentially carbonless alloys of substantial strength can be made by pressing and sintering appropriate mixtures of nickel and iron powders. The 20 per cent nickel, 80 per cent iron alloy showed the highest strength, 106,000 lb. per sq. in., and 4.3 per cent elongation after pressing and sintering twice. This high strength is probably a reflection of

the gamma to alpha transformation in the nickel-iron system, which produces a substantial increase in strength even in low-carbon alloys. The effect of carbon in strengthening sintered and heat-treated nickel-iron alloys also has been studied and will be reported shortly. A comparison of the properties obtained by mixing the component elements and sintering to effect diffusion with those resulting from pressing and sintering alloyed powders offers a field for future investigation.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to The International Nickel Company, Inc. for supporting this research, and to N. B. Pilling, Director of Research Laboratory, The International Nickel Company, Inc., Prof. G. J. Comstock and Prof. J. F. Kuzmick, Department of Powder Metallurgy, Stevens Institute of Technology, under whose supervision this work was undertaken, for their guidance, their assistance, and generous support in supplying laboratory facilities. The authors extend their thanks also to Mr. E. M. Wise, of The International Nickel Company, Inc., for his helpful suggestions in reviewing this paper.

DISCUSSION

(*W. R. Toeplitz presiding*)

JOHN WULFF.*—On the curves it seemed that the 20 per cent nickel addition gave the best mechanical properties. In looking over your data, it occurred to me that perhaps a small percentage of extreme fines of carbonyl nickel, for example, might improve the physical properties of the sintered compact.

AARON FINGER (author's reply).—It is our belief that the high values of hardness and tensile strength when the nickel content is between 15 and 20 per cent are primarily a function of the composition. Investigators

* Professor of Metallurgy, Massachusetts Institute of Technology, Cambridge, Massachusetts.

whose work was reviewed by Marsh* reported that alloys in the same composition range made by conventional methods showed similar marked increases. According to published works, the increase in strength is due to the presence of a martensite-like constituent that results from the gamma-alpha transformation. If we had used carbonyl nickel, it is possible that higher values would have been obtained, but the maximum would still occur when the nickel content is between 15 and 20 per cent.

JOHN WULFF.—I agree in general with the author that the alloy composition is the salient factor in producing compacts of such good mechanical properties. My previous remarks pertain primarily to the more rapid diffusion possible when extreme fines are employed.

R. P. SEELIG.†—I think the authors ought to be congratulated on their excellent and very thorough study of this iron-nickel system. I happen to know they have done some work on the nickel-copper system, and I wonder if they would care to say anything about it, for comparison?

AARON FINGER.—The work on nickel and copper was done independently of the work on nickel and iron. Its purpose was to get some of the properties of Monel metal and cupronickel. As we added nickel to pure copper, however, the physical properties were not materially improved, nor was there any particular range of composition in which a marked change was noted. In general, with the exception of the high-nickel compositions, the addition of nickel to copper did not improve the properties of the latter. Even repressing, or repressing and resintering, did not cause any outstanding improvement. In the alloys of iron and nickel, on the other hand, remarkable changes in properties were produced by varying the composition alone. It is possible, of course, that alloys of copper and nickel with better properties could be produced with different powders.

The change in properties of the iron-nickel alloys with composition differs from the change produced by the addition of copper to iron. The properties of the former alloys are due

to the mutual diffusion of the constituents in the solid state; the latter material owes its strength to the brazing action of the copper, which melts during sintering.

F. V. LENEL.—Do I understand that you attribute some of the good properties to the incomplete diffusion of the iron and nickel?

AARON FINGER.—No, it is not a question of incomplete diffusion, because the alloys made by casting, in which the metals may be assumed to be intimately mixed, show the same effect of composition. The properties probably are due to a martensite-like structure that forms during the gamma to alpha phase change.

F. V. LENEL.—Have you investigated the cause of the variation of time and difference of sintering time on the properties?

AARON FINGER.—No, we did not do that. However, we prepared steels containing nickel, sintering them for one hour only. We added up to 7 per cent carbonyl nickel and obtained tensile strengths of the order of 110,000 to 115,000 lb. per sq. in. without heat-treating. The microstructure consisted of cores of martensite in a matrix of ferrite and pearlite.

GEORGE STERN.*—The author mentioned that future work would include work on prealloyed powders, and I have a question to ask about this. We have tried using a prealloyed powder, essentially 50 per cent iron, 50 per cent nickel. In regular wrought materials this composition can be annealed and rendered quite soft. However, we have tried pressing this material in the as-received condition, and as annealed, and the pressing and sintering of these prealloyed powders could be accomplished only with great difficulty. I wonder if the authors have had any experience with this 50-50 Fe-Ni alloy?

AARON FINGER.—No, we have not used that. A different nickel powder might give better results. Commercially available powders were used so that the work could be repeated at any time. Nickel from Metals Disintegrating Co. (MD-151) and electrolytic iron from Plastic Metals were used. We have not used prealloyed powders in this work at all.

* Alloys of Iron and Nickel, I. A.S.M. Monograph, New York, 1938. McGraw-Hill Book Co.

† Powder Metallurgy Incorporated, Long Island City, N. Y.; American Electro Metallurgical Corporation, Yonkers, New York.

* American Electro Metals Corporation, Yonkers, New York.

Effect of Rolling and Annealing upon the
Crystallography, Metallography
and Physical Properties of
Copper Strip

Effect of Rolling and Annealing upon the Crystallography, Metallography, and Physical Properties of Copper Strip

BY WILLIAM M. BALDWIN, JR.*

(New York Meeting, February 1942)

WELL known to every metallurgist is the fact that different production schedules will profoundly affect the character of annealed metal strip. Yet the number of conditions

should not be dismissed as being too impractical, for the crystallographic condition existing within the metal is a principal influence upon both the external mechanical

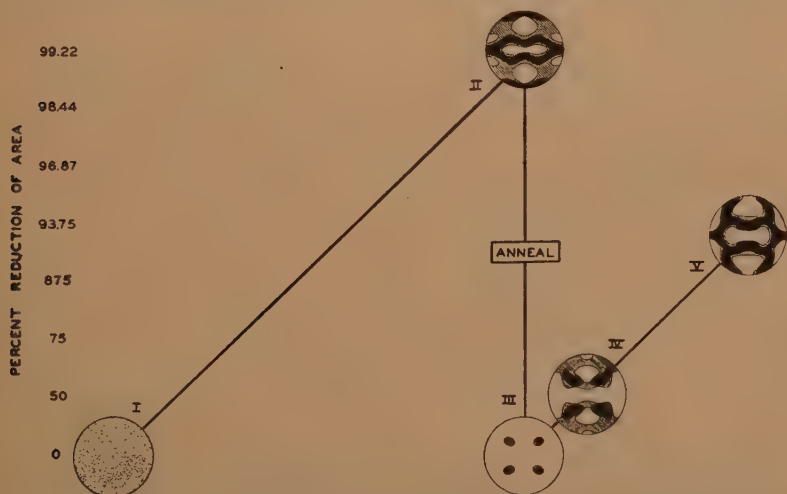


FIG. 1.—SCHEMATIC "MAP" OF CRYSTALLOGRAPHIC BEHAVIOR OF COPPER WHEN VARIOUSLY ROLLED AND ANNEALED.

that may be wrought by different combinations of rolling and annealing schedules is so myriad that despite the continual research that is being applied to this subject, the complete picture is not yet known.

Copper, like all other metals, during the process of rolling or annealing, develops certain crystallographic configurations which

properties and the behavior of the material when it is subjected to such operations as bending, flanging, drawing, and so forth.

EFFECT OF ROLLING AND ANNEALING UPON THE CRYSTALLOGRAPHY OF COPPER STRIP

The most salient points in the crystallographic reactions of polycrystalline copper to rolling and annealing may be best represented graphically by a "map" such as that given in Fig. 1.

- I. As copper strip is cold-rolled from a randomly oriented structure (pole figure I),

Manuscript received at the office of the Institute Nov. 6, 1941. Issued as T. P. 1455 in METALS TECHNOLOGY, April 1942. This paper was withheld from TRANSACTIONS volume in 1942 (Vol. 147) by request of the Office of Scientific Research and Development.

* Research Metallurgist, Cleveland Mill Division, Chase Brass and Copper Co., Cleveland, Ohio.

a preferred orientation is built up within the metal, which, when the sheet is severely cold-rolled, becomes quite characteristic and clearly defined. This cold-rolled

strip is annealed, the recrystallization texture is almost completely cubically aligned, as is shown in pole figure III (again from Brick and Williamson).

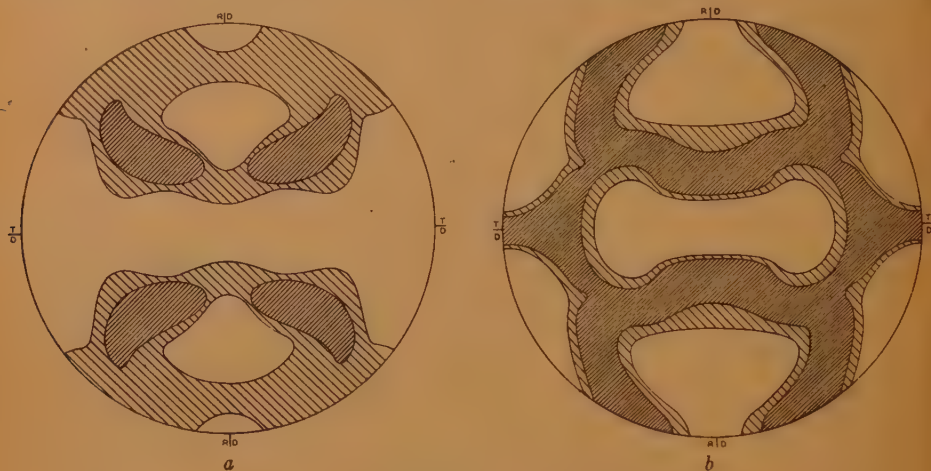


FIG. 2.—POLE FIGURES OF COPPER STRIP.

a. Rolled 53.5 per cent from a totally cubically aligned structure.

b. Rolled 91 per cent from a totally cubically aligned structure.

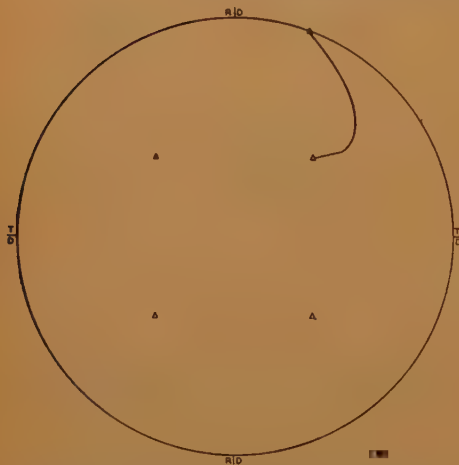


FIG. 3a.—“AVERAGE” MIGRATORY PATH OF ONE OCTAHEDRAL POLE (TAKEN FROM FIG. 2b).

structure has been reported most recently and completely by Brick and Williamson,¹ whose pole figure for copper strip cold-rolled 99 per cent is given as pole figure II.

2. When such severely cold-rolled copper

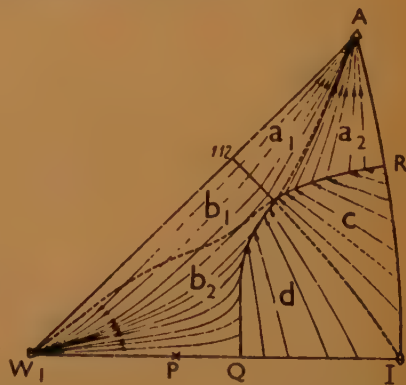


FIG. 3b.—BOAS AND SCHMID'S DIAGRAM FOR MIGRATION OF AXIS OF TENSION.

For compression the arrows are to be reversed.

3. Should soft copper strip with a totally cubically aligned structure be further cold-rolled, the rolling textures developed are as shown in pole figures IV and V in Fig. 1, and in greater detail in Fig. 2. These pole figures were obtained as follows: A hot-rolled silver-bearing copper bar (of the analysis shown in Table 1) of 2.0-in. gauge

¹ References are at the end of the paper.

was cold-rolled to 0.043-in. gauge (a reduction of 95.5 per cent) and then annealed at 538°C. (1000°F.). This treatment produced a strip of totally cubically aligned structure (Fig. 5). This material was rolled to (a) a nominal 0.021-in. gauge (an actual reduction of 53 per cent) and (b) a nominal 0.004-in. gauge (an actual reduction of 91 per cent). These two strips were pickled to 0.001-in. gauge and subjected to X-ray

this migration is occurring may be seen in Fig. 3a, where the "average" path taken from Fig. 2b of one octahedral pole from its ideal (100) [100] position to its

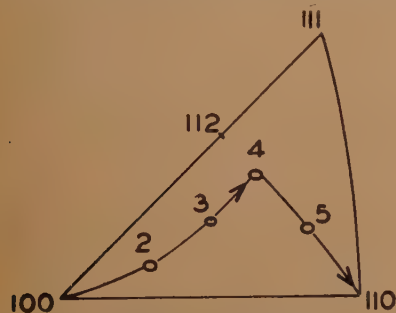


FIG. 3c.—"AVERAGE" MIGRATORY PATH OF COMPRESSION AXIS.

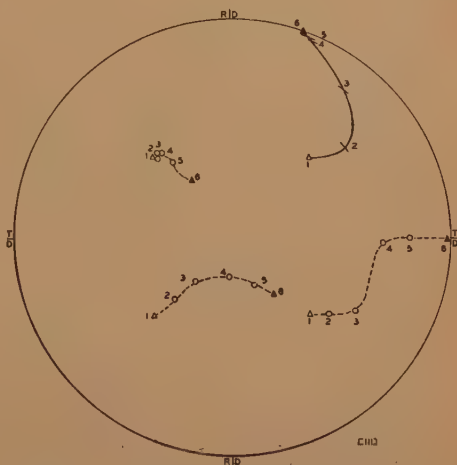


FIG. 3d.—MIGRATORY PATHS OF ALL FOUR OCTAHEDRAL POLES.

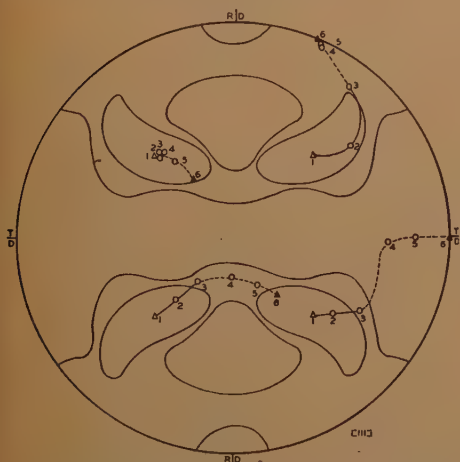


FIG. 3e.—SUPERIMPOSITION OF FIG. 3d UPON 2a.

analysis. The resulting pole figures are given in Figs. 2a and 2b. It is clearly seen that there is a migration of the octahedral poles from the four ideal locations occupied in the annealed state toward such positions as would form the original cold-rolled textural pattern. The very path over which

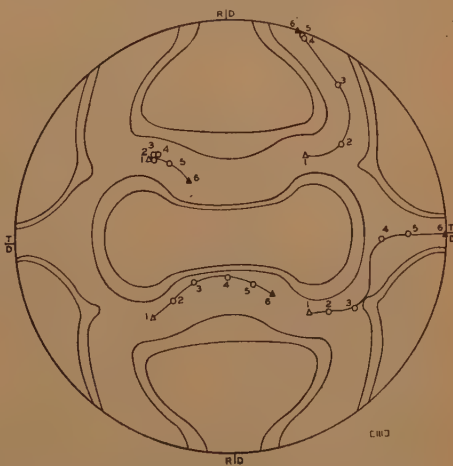


FIG. 3f.—SUPERIMPOSITION OF FIG. 3d UPON 2b.

ideal (100) [112] end position is reproduced. From this path and the "average" theoretical path of the migration of the rolling plane as postulated by Boas and Schmid,² it is possible to calculate the paths that the other three octahedral poles should follow. This has been done for six positions along Boas and Schmid's theoretical path. The

resulting three paths are given in Fig. 3*d*. How well they coincide with the pole figures is shown in Figs. 3*e* and 3*f*, where the paths have been superimposed upon the

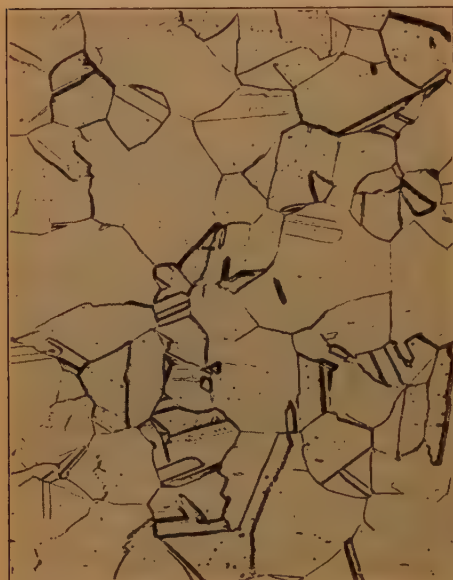


FIG. 4.—RANDOMLY ORIENTED ANNEALED COPPER STRIP. $\times 75$.
Ammonium hydroxide-hydrogen peroxide etch.

pole figures. Not only is the coincidence apparent for Fig. 3*f*, where migration is fully developed, but also in Fig. 3*e*, where migration is still in an early stage. The

TABLE I.—*Chemical Analysis of Copper Investigated**

Element	Silver-bearing	Electrolytic Tough-pitch
Copper.....	99.96	99.93
Silver.....	0.038	0.002
Lead.....	Less than 0.05	Less than 0.05
Iron.....	0.01	0.01
Phosphorus.....	Less than 0.001	Less than 0.001
Silicon.....	Less than 0.01	

* No gold, bismuth, zinc, cobalt, tellurium, aluminum, tin, or cadmium was detected spectrographically in either of the cakes.

paths shown in Fig. 3*d* indicate that in the migration of the crystals rotation occurs about the upper left-hand octahedral pole until position four—approximately—is reached, at which point rotation occurs around the upper right-hand octahedral

pole. This behavior affects the recrystallization of this type of strip, in a manner described in the next section.

The reaction of copper in all three phases described is similar to the behavior of iron-nickel alloys. (Pawlek,³ Wassermann,⁴ Sachs and Spretnak.⁵)

METALLOGRAPHY OF SOFT COPPER SHEET

The metallographic appearance of statistically randomly oriented copper (pole figure I) is well known to the metallurgist. A representative photomicrograph of such copper is reproduced in Fig. 4. In Fig. 5, the photomicrographs of totally cubically aligned copper are given. Fig. 5*a* shows the appearance of silver-bearing copper cold-rolled from 2.0 to 0.043-in. and annealed at 1000°F., when etched with ammonium hydroxide-hydrogen peroxide. No grain boundaries are observed and little of the microstructure except strung-out oxide particles is discernible. Fig. 5*b* is the same specimen etched with an aqueous solution of ammonium persulphate. Square Tamman etch pits have begun to develop and slight traces of grain boundaries are visible. Fig. 5*c* is still the same specimen treated more heavily with an aqueous solution of ammonium persulphate. The two features seen in Fig. 5*b* now appear in bolder form; the etch pits cover the entire grain surfaces and the grain boundaries have become deep chasms.

When copper is rolled to any temper less severe than that represented by pole figure II and is then annealed, the resulting microstructure, while not totally cubically aligned (as represented by pole figure III), still contains a certain percentage of cubically aligned grains.

Such a condition is shown in Fig. 6, a photomicrograph of silver-bearing copper rolled from 0.512-in. gauge to 0.043-in. gauge (92 per cent reduction) and annealed at 1000°F. The etchant is ammonium hydroxide-hydrogen peroxide.

The general matrix of the metal is cubically aligned. This may be seen from

the direction of the two sets of twin blocks, which run in a direction of plus 45° and minus 45° , respectively, to the direction of rolling, and at right angles to each other.

of the matrix as being cubically aligned. This is shown graphically in Fig. 6c. Attention is drawn to the fact that the etchant has still failed to bring out the

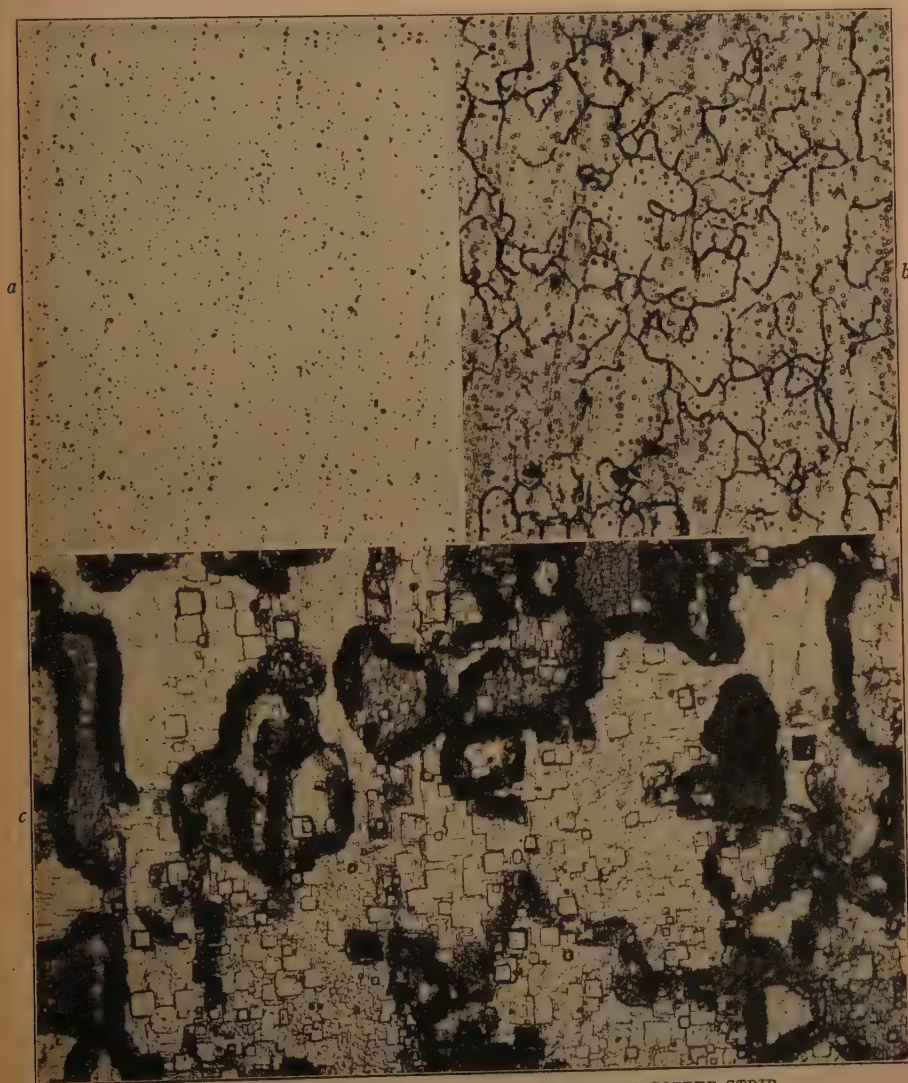


FIG. 5.—TOTALLY CUBICALLY ALIGNED ANNEALED COPPER STRIP.

- a.* Ammonium hydroxide-hydrogen peroxide etch. $\times 75$.
b. 20 per cent aqueous solution of ammonium persulphate etch. Ten seconds immersion. $\times 75$.
c. 20 per cent aqueous solution of ammonium persulphate etch. Two minutes immersion. $\times 250$.

Since the recrystallization twins of copper normally are the octahedral planes (cf. Mathewson,⁶ Phillips⁷ et al.), the directions of these twin blocks place the orientation

grain boundaries in the cubically aligned matrix. Appearing in this picture, also, is a fairly large grain (about 0.600 mm. long, 0.200 mm. wide) whose orientation may

likewise be derived by its three sets of twin traces, which form angles of 0° , $70^\circ 32'$, and $54^\circ 35'$ with the direction of rolling and thus place its orientation as

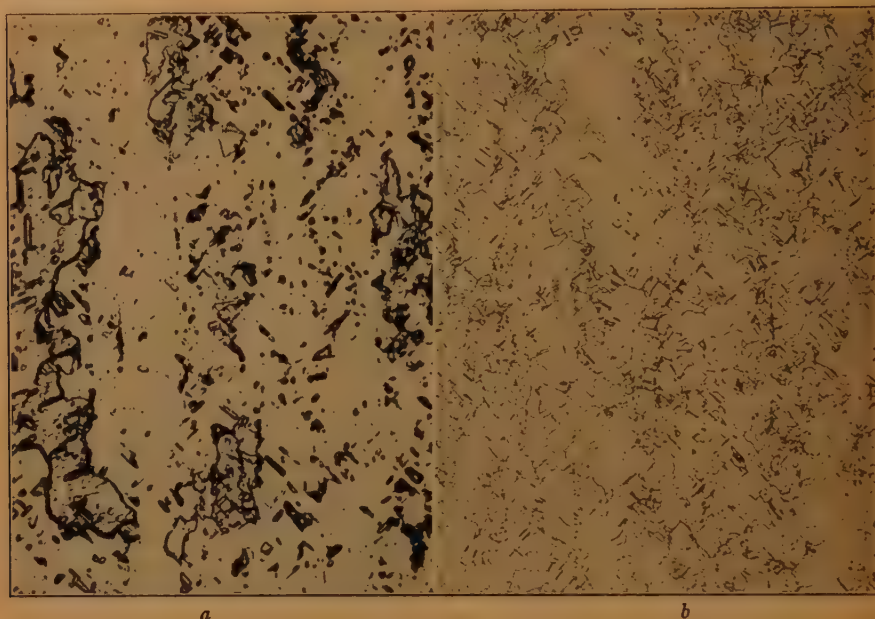


FIG. 6a.—PARTLY CUBICALLY ALIGNED ANNEALED COPPER STRIP. $\times 75$.

Ammonium hydroxide-hydrogen peroxide etch. Orientation of grain in center is $(110) [112]$; surrounding matrix, $(100) 001$.

FIG. 6b.—ANNEALED COPPER STRIP CONTAINING EVEN LESS CUBICALLY ALIGNED GRAINS THAN STRIP SHOWN IN 6a.

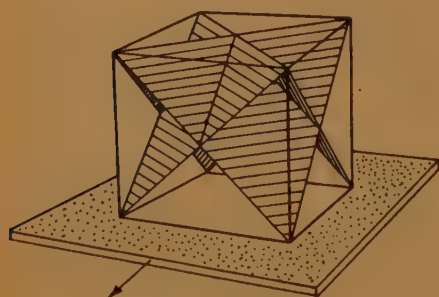


FIG. 6c.—GRAPHIC PRESENTATION OF REASON FOR APPEARANCE OF TWINS OF CUBICALLY ALIGNED GRAINS.

The metal strip is shown, its rolling plane speckled, its rolling direction indicated by an arrow. Superimposed upon the strip is the unit cell of the copper crystal in its appropriate cubically aligned orientation. Within the cube are sketched the four twinning planes (octahedral, or $\{111\}$ planes) with intercepts on the upper plane (plane of micrograph) at 45° to the rolling direction and at 90° to each other.

being $(110) [112]$. This is a holdover from the main rolling texture orientation. This orientation has been noticed by Cook and Richards.⁸ Fig. 6b is a photomicrograph in the rolling plane of a copper strip rolled from 0.512 to 0.064-in. and annealed at 1000°F . This shows several grains scattered throughout the microstructure, which are cubically aligned. In like manner, these grains may be recognized by the distinctive directions in which the two sets of twins lie.

Fig. 7 shows how two microstructures that are not totally cubically aligned appear when etched with ammonium persulphate. The cubically aligned grains in both instances appear white; those grains of other orientations appear black.

An etchant that attacks copper in a manner similar to the way in which

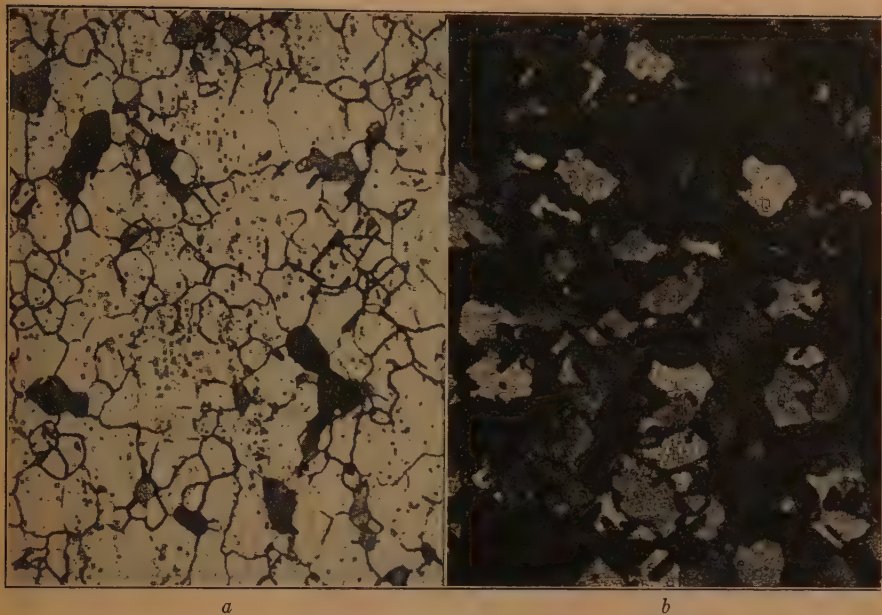


FIG. 7.—PARTLY CUBICALLY ALIGNED ANNEALED COPPER STRIPS. $\times 75$.
20 per cent aqueous solution of ammonium persulfate white grains are cubically aligned;
dark grains have other orientations.

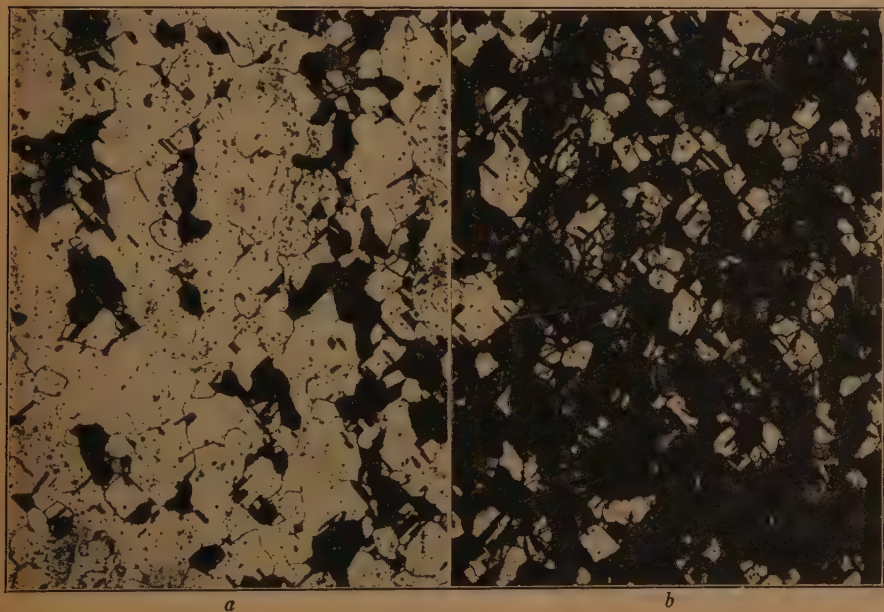


FIG. 8.—PARTLY CUBICALLY ALIGNED ANNEALED COPPER STRIP. $\times 75$.
Acidic aqueous solution of ferric chloride etch.



FIG. 9.—TYPICAL SERIES OF COPPER STRIP ROLLED DIFFERENT DEGREES AND THEN ANNEALED AT A CONSTANT TEMPERATURE.

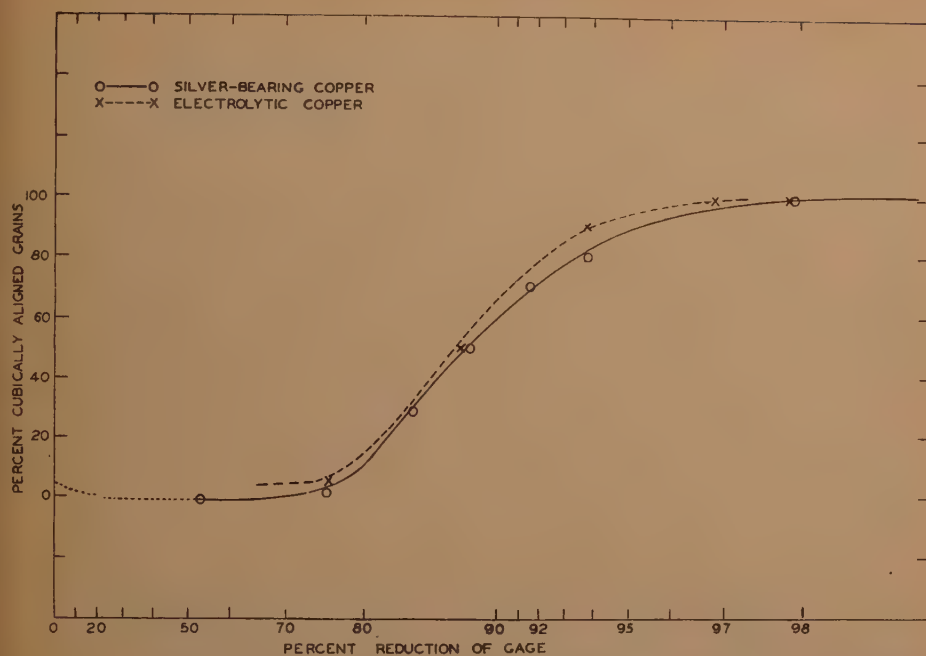


FIG. 10.—VARIATION OF PERCENTAGE OF CUBICALLY ALIGNED GRAINS WITH PREVIOUS REDUCTION BY ROLLING FOR ANNEALED ELECTROLYTIC AND SILVER-BEARING COPPER STRIP STARTING WITH A HOT-ROLLED STRUCTURE.

Annealing temperature, 750° . Original stock, 0.512-in. gauge hot-rolled copper.

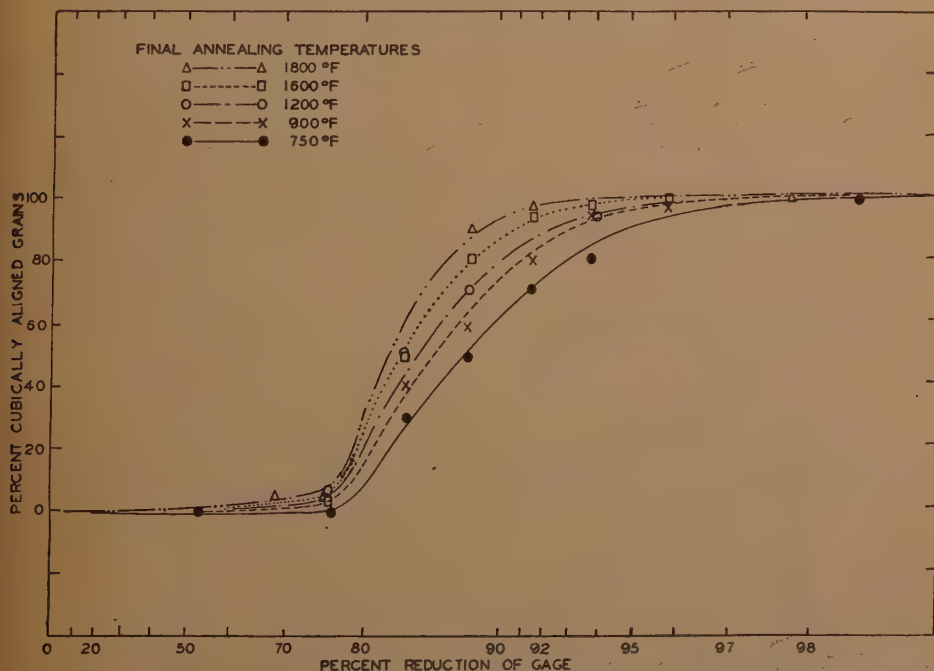


FIG. 11.—VARIATION OF PERCENTAGE OF CUBICALLY ALIGNED GRAINS WITH PREVIOUS REDUCTIONS BY ROLLING FOR ANNEALED SILVER-BEARING COPPER WITH DIFFERENT FINAL ANNEALS. HOT ROLLED STARTING STRUCTURE, 0.512 IN. GAUGE.

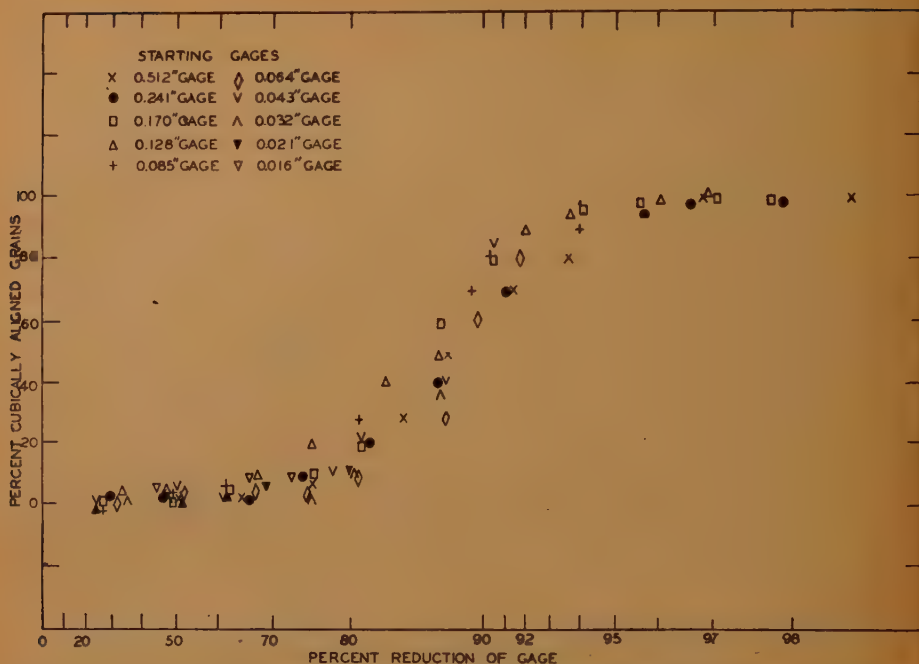


FIG. 12.—VARIATION OF PERCENTAGE OF CUBICALLY ALIGNED GRAINS WITH PREVIOUS REDUCTIONS BY ROLLING FOR ANNEALED SILVER-BEARING COPPER STARTING WITH AN ANNEALED STRUCTURE OF NEGLIGIBLE CUBIC ALIGNMENT. R.F. ANNEAL, 1000°F.; FINAL ANNEAL, 750°F.

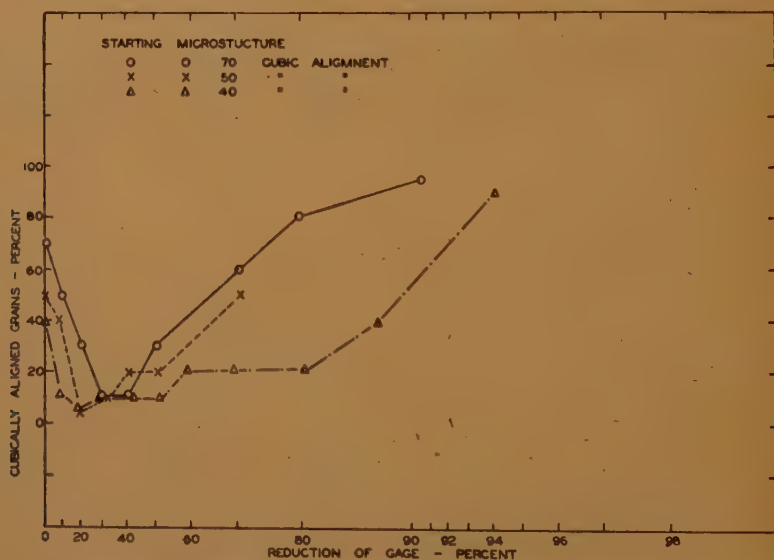
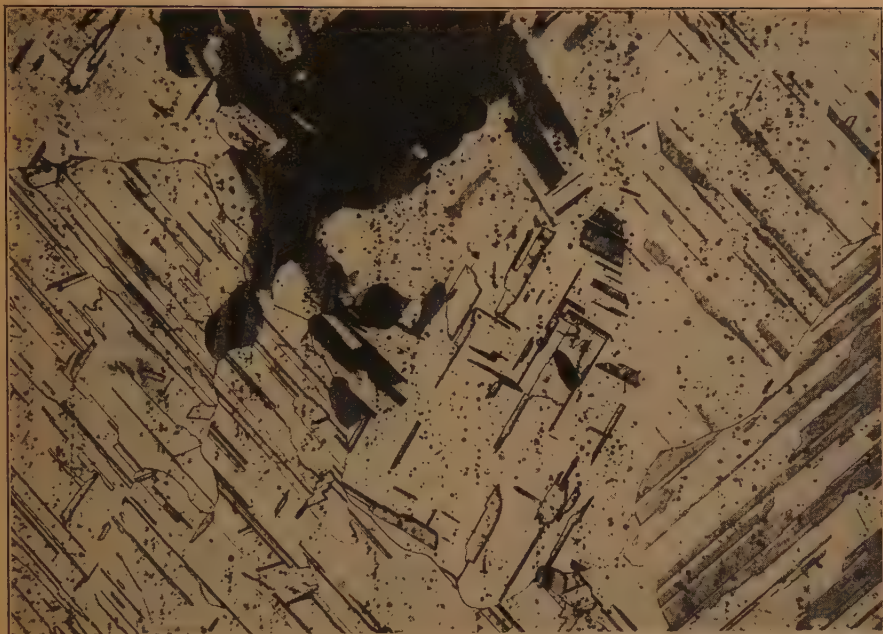
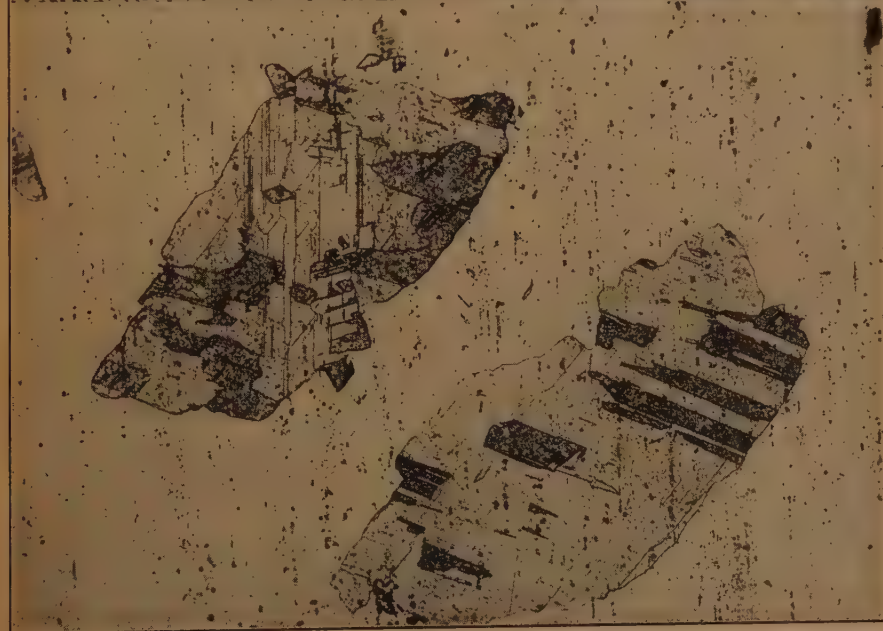


FIG. 13.—VARIATION OF PERCENTAGE OF CUBICALLY ALIGNED GRAINS WITH PREVIOUS REDUCTIONS BY ROLLING FOR ANNEALED SILVER-BEARING COPPER STARTING WITH ANNEALED STRUCTURE OF DIFFERENT PERCENTAGE OF CUBICALLY ALIGNED GRAINS. R.F. ANNEAL, 1200°F.; FINAL ANNEAL, 1200°F.



14



15

FIG. 14.—ANNEALED COPPER STRIP PREVIOUSLY ROLLED 22 PER CENT FROM TOTALLY CUBICALLY ALIGNED STRUCTURE. $\times 75$.

Ammonium hydroxide—hydrogen peroxide. R.F. anneal, 1000°F .; final anneal, 1000°F .

FIG. 15.—BEGINNING OF RECRYSTALLIZATION OF SPECIMEN SHOWN IN FIG. 14.

ammonium persulphate does—i.e., eats out the metal along its cubic planes—is ferric chloride (see Barrett and Levensen⁹). If, however, copper is exposed to the

aligned grains was estimated from actual specimens by three different operators and the percentage of cubically aligned grains was assigned to the nearest one of the



FIG. 16.—POLE FIGURE (111) PLANES OF 45 GRAINS OF SPECIMEN SHOWN IN FIG. 14.

etchant for but a short interval of time, those grains not cubically aligned are preferentially oxidized, so that a black and white contrast of a very sharp nature is obtained. The maximum variation from the ideal (001) [100] orientation at which the grains still appear white was 18° , as determined by twin traces. Two pictures of metal etched with ferric chloride for a short interval of time are reproduced in Fig. 8.

This last etch, because it produced a picture that is both clear and sharp, offers a means of quantitatively estimating the percentage of cubically aligned grains present in a given microstructure. The variation of the percentage of cubically aligned grains with the severity of cold-rolling was determined in exactly this manner. A series of specimens was rolled various amounts from hot-rolled copper, annealed, and then etched with the ferric chloride contrast etch. Such a series is presented in Fig. 9 (the last three were etched with ammonium persulphate). The percentage of cubically

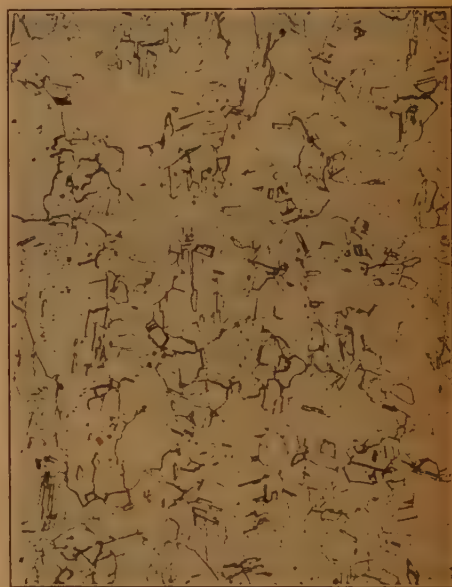


FIG. 17.—ANNEALED COPPER STRIP ROLLED 81 PER CENT FROM TOTALLY CUBICALLY ALIGNED STRUCTURE. R.F. ANNEAL, 1000°F .; FINAL ANNEAL, 1000°F .

following arbitrary values: 0, 1, 2, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 95, 98, 99, or 100 per cent since no greater accuracy than 10 per cent could be had in estimating in the middle ranges and one or two per cent in the end ranges. Estimates by the three men never varied more than plus or minus one classification: the reproducibility of this technique was accurate to within these limits.

Figs. 10 to 13 show the variation of cubically aligned grains with percentage of reduction previous to the final anneal for different conditions. The percentage of grains appearing as white (i.e. the percentage of grains whose (100) plane lies within 18° of the rolling plane) for a randomly oriented specimen would be 14.7 per cent; but the number of grains whose (100) plane

not only lies within 18° of the rolling plane but whose (100) axis lies within 18° of the rolling direction is 4.1 per cent. This percentage is given for the hot-rolled

15 shows the beginning of recrystallization: few nuclei have formed.) These huge grains are freely and distinctly twinned, and this characteristic allows determination

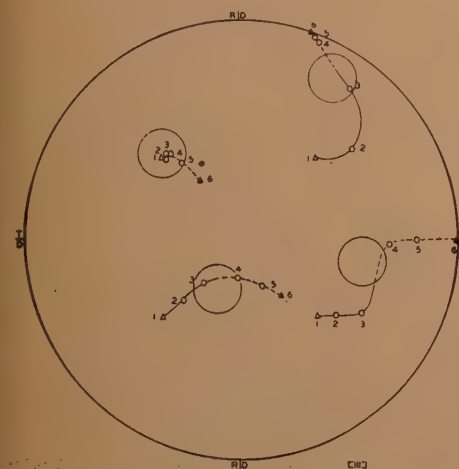


FIG. 18a.—SUPERIMPOSITION OF ONE SET OF RECRYSTALLIZED POLES FROM FIG. 16 ON FIG. 3d.

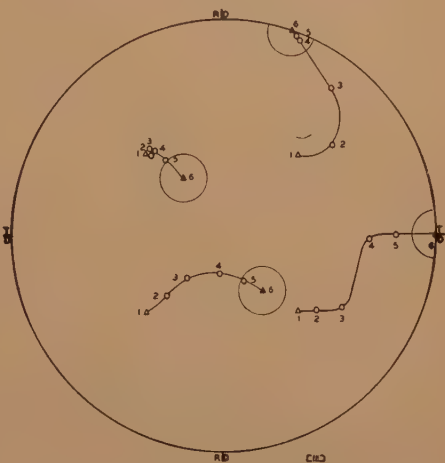


FIG. 18b.—SUPERIMPOSITION OF ONE SET OF OCTAHEDRAL POLES OF (110) 112 ORIENTATION ON FIG. 3d.

specimens. In Fig. 10, the initial condition of the metal was hot-rolled, two different analyses of copper being represented, all anneals being carried out at a constant temperature. In Fig. 11, the initial condition of the metal was hot-rolled. Only one analysis is represented but different anneals have been used. In Fig. 12, the initial condition of the metal was cold-rolled and annealed but contained little or no cubically aligned grains. In Fig. 13, the initial condition of the metal was cold-rolled and annealed and contained various percentages of cubically aligned grains.

The "map" in Fig. 1, shows that if a totally cubically aligned annealed structure is further cold-rolled, the cubically aligned structure is retained at first almost completely but gradually decomposes into other orientations. What occurs when this material is annealed is shown in Figs. 14 to 18. At 22 per cent reduction (Fig. 14) the grain sizes developed are huge, running as large as a centimeter or two at times. (Fig.

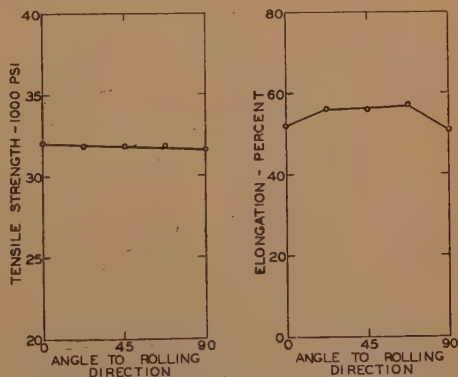


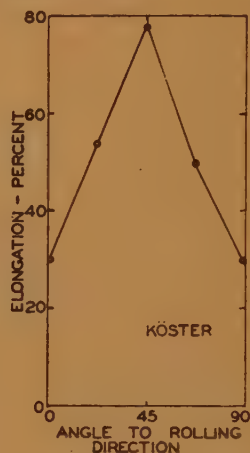
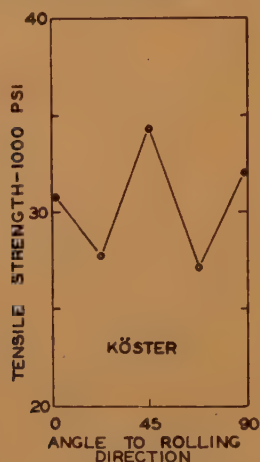
FIG. 19.—TENSILE STRENGTH AND ELONGATION AT VARIOUS ANGLES TO ROLLING DIRECTION OF HOT-ROLLED COPPER.

of their orientation by stereographic means (Barrett¹⁰). Fig. 16 is a pole figure of the octahedral poles of 45 grains of their type. The poles lie close to positions best described as

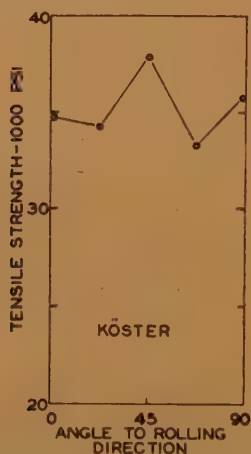
R.P.	R.D.
($\bar{1}13$)	Between $[110]$ and $[301]$ 21° from $[301]$
($\bar{1}13$)	Between $[301]$ and $[2\bar{1}1]$ 10° from $[301]$

These two orientations are twins of one another. Among the 45 grains, two were noticed whose orientations were

interesting. The findings of Sachs and Spretnak⁵ and of Brick and Williamson¹ show that in an iron-nickel alloy and cop-



a. Cathode copper strip, hydrogen 0.00012 per cent, rolled 93 per cent, annealed 600°C. (Köster)



b. Cathode copper strip, hydrogen 0.00026 per cent, rolled 93 per cent, annealed 600°C. (Köster).

FIG. 20.—DIRECTIONALITY OF TENSILE PROPERTIES OF ANNEALED COPPER

R.P. R.D.
(115) Between [551] and [501] 2° from [501]

And yet another whose orientation was

R.P. R.D.
(100) 14° from [001]

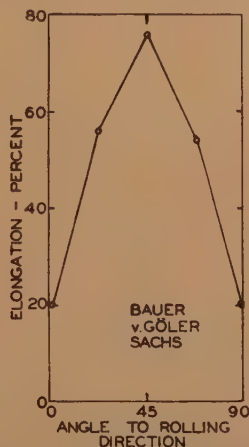
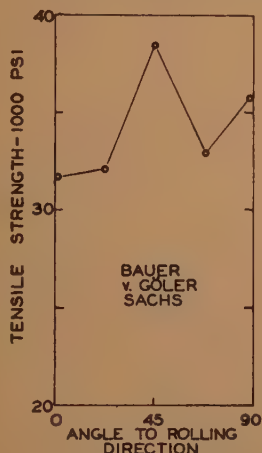
The orientations of three grains could not be determined because of an insufficient number of sets of twin traces.

This mode of recrystallization is highly

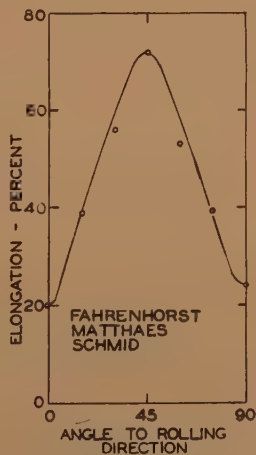
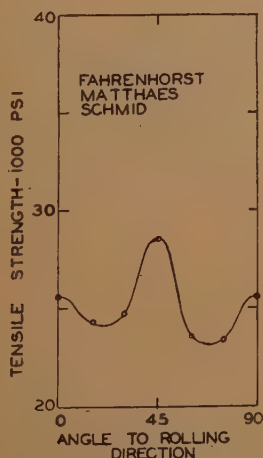
per, respectively, when cold-rolled severely from a random orientation, the minor constituent of the rolling texture, (100) [100], forms the nucleation and rolling textures upon recrystallization. In the present case, where the (100) [100] orientation is the major rolling texture, it notably fails to appear in the recrystallization texture. It is apparent that nucleation does

not follow the dictate of some particular and constant orientation; rather, nucleation results from the orientation in the

when the metal has been rolled 81 and 91 per cent. This may be seen from the prevalence of twins running in a direction



c. Electrolytic copper strip, rolled 92.5 per cent, annealed 500°C. (Bauer, v. Göler and Sachs).



d. Electrolytic copper strip, rolled 96 per cent, annealed 500°F.

CONTAINING VERY HIGH PERCENTAGES OF CUBICALLY ALIGNED GRAINS.

metal that represents some minimum or maximum quantity (such as energy)—a stationary quantity as conceived in the theory of calculus of variations.

This fact may be deduced, again, from the microstructures of copper rolled higher amounts with a starting structure of totally cubically aligned soft copper (Fig. 17). A distinct preferred orientation is present

closely parallel to the rolling direction, at 70° to the rolling direction, and at approximately 55° to the rolling direction. This condition is different from the orientation represented in Fig. 16: a second transmutation has taken place. The angles of these twin directions indicate that the orientation into which this strip has almost completely recrystallized is the (110) [112] position.

A comparison of the textural patterns of the rolled and annealed states may now be made. In copper strip that has been cold-rolled 91 per cent (Fig. 2*b*), the migration of

on the paths of migration, and at a point that is only part of the way along the path. It is reasonable to assume that these were the most advanced poles in the rolled state,

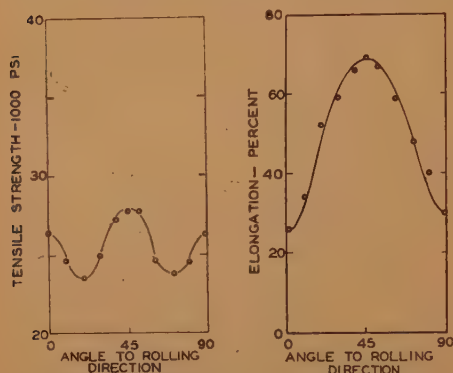


FIG. 21.—DIRECTIONALITY OF TENSILE PROPERTIES OF SILVER-BEARING COPPER WITH TOTAL CUBIC ALIGNMENT.

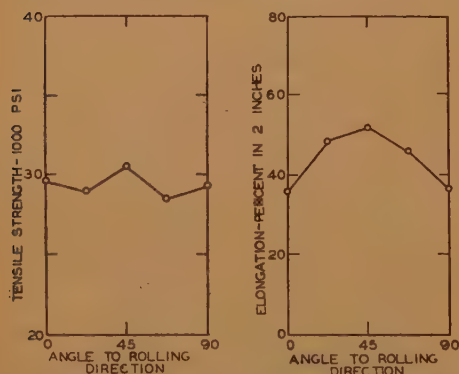


FIG. 23.—DIRECTIONALITY OF TENSILE PROPERTIES OF SILVER-BEARING COPPER WITH 80 PER CENT CUBIC ALIGNMENT.

octahedral poles is in full progress; the end position, (110) [112], is well populated. Upon recrystallization, these most advanced positions have acted as nuclei, and the annealed metal is composed of grains of this orientation. In copper strip that has been cold-rolled 22 per cent, the migration of octahedral poles is just developing—the poles have traversed only a portion of their respective paths. Superimposition of pole figure 16 upon Fig. 3*d* shows that the primary recrystallized poles do indeed fall

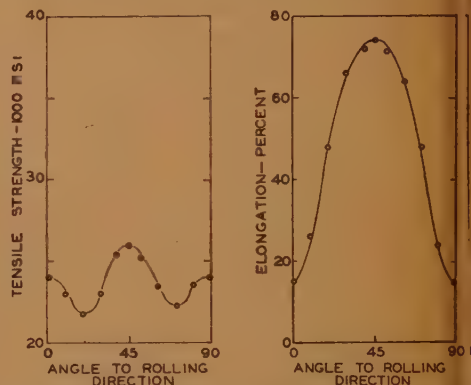


FIG. 22.—DIRECTIONALITY OF TENSILE PROPERTIES OF ELECTROLYTIC COPPER WITH TOTAL CUBIC ALIGNMENT.

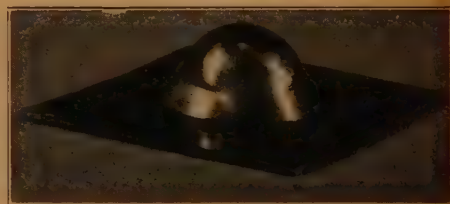


FIG. 24.—ERICHSEN CUP TEST OF ELECTROLYTIC COPPER OF 100 PER CENT CUBIC ALIGNMENT.

since the pole figure of material rolled 53.5 per cent is only slightly more advanced.

REACTIONS OF MECHANICAL PROPERTIES

Randomly oriented copper should theoretically possess equal properties in all directions. True hot-rolled copper approaches this ideal condition. Fig. 19 shows the tensile strength and elongation of hot-rolled copper. The properties tend to become identical in all directions. The properties of totally cubically aligned annealed copper strip, on the other hand, because the orientation is so pure, vary markedly and in a characteristic manner. A number of investigators have reported the directional properties of this orienta-

tion. Reproduced in Fig. 20 are the results of Köster,¹¹ Bauer, v. Goler and Sachs,¹² Fahrenhorst, Matthes and Schmid,¹³ for copper that has been rolled extreme

Köster's curves for copper that is hydrogen-rich and hydrogen-poor, and from the curves developed in this research for electrolytic and silver-bearing copper.

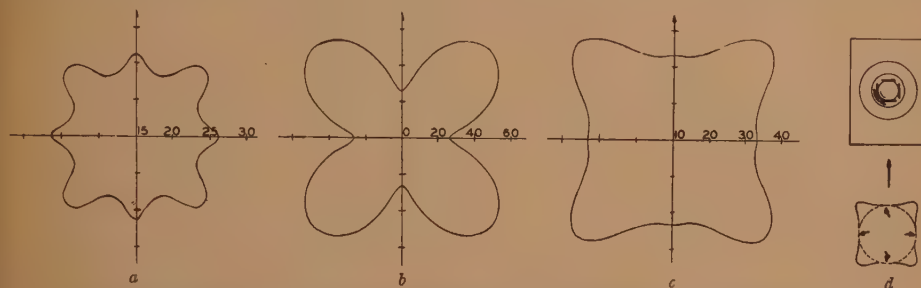


FIG. 25.—DIRECTIONALITY OF TENSILE PROPERTIES OF ELECTROLYTIC COPPER OF 100 PER CENT CUBIC ALIGNMENT AS A BASIS FOR ERICHSEN CUP TEARS SHOWN IN FIG. 28.

a, tensile strength; *b*, elongation; *c*, true tensile strength; *d*, stress analysis of Erichsen cup.

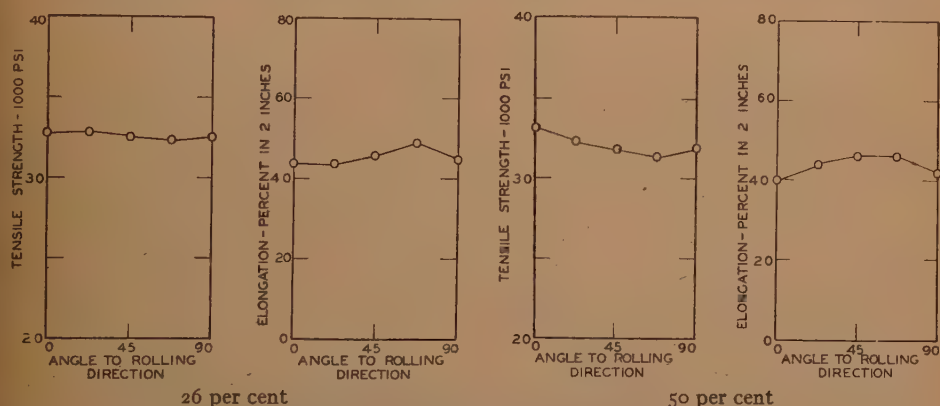


FIG. 26.—DIRECTIONALITY OF TENSILE PROPERTIES OF ANNEALED COPPER STRIP WITH SMALL PERCENTAGES OF CUBICALLY ALIGNED METAL.

amounts—in the range of 93 to 98 per cent—and annealed.

In this investigation two compositions of copper—silver-bearing and tough-pitch electrolytic—with 100 per cent cubically aligned microstructure were tested at 0°, 10°, 20°, 30°, 40°, 45°, 50°, 60°, 70°, 80°, 90° to the direction of rolling (Figs. 21 and 22).

The actual values of tensile strength and elongation as reported by the various authors and in this investigation do not coincide; but the shapes of the curves follow the same pattern. The influence of impurities upon the actual values of these properties is strong, as may be seen from

Grain size, also, will affect the actual values obtained. But the shape of the curves is a function of the orientation of the strip. The correspondence of the form of these curves to those for a single crystal of copper (Czochralski¹⁴) has already been pointed out by Köster.¹¹

The distinctive shape of these curves is not peculiar to microstructures of 100 per cent cubically aligned textures but occurs also for copper containing percentages of cubically aligned grains down to roughly 70 per cent. Thus, the same distinctive curve of tensile strength and elongation is noticed for copper strip that has been rolled 16

B. and S. gauge numbers, and which when annealed contained but 80 per cent cubi-

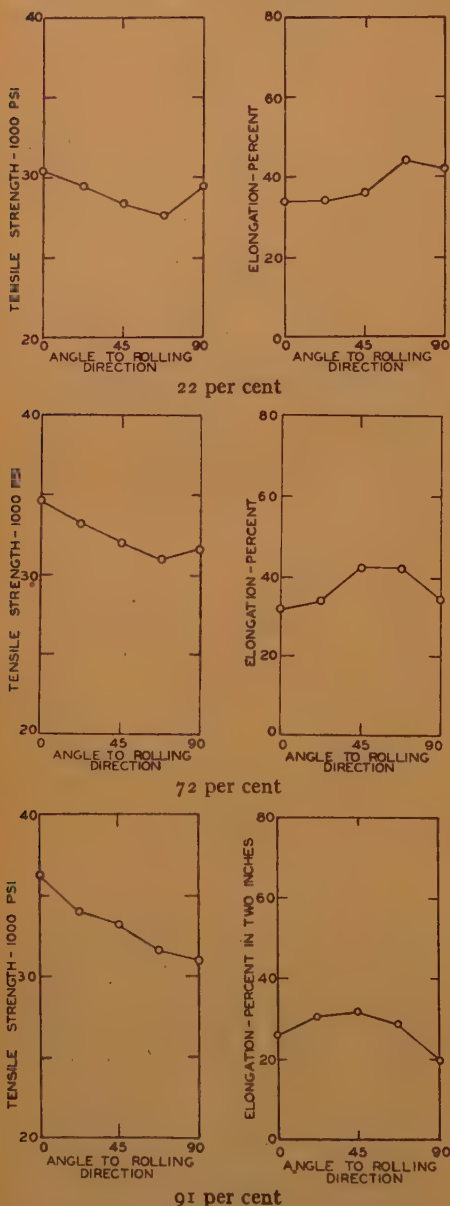


FIG. 27.—DIRECTIONALITY OF TENSILE PROPERTIES OF ANNEALED COPPER STRIP ROLLED FROM TOTALLY CUBICALLY ALIGNED MATERIAL.

cally aligned grains (Fig 23). The minimum critical percentage of cubically aligned

grains that give rise to this type of curve is not definite. Some specimens that contained as low as 60 per cent cubically aligned grains yielded this type of curve; other specimens of the same percentage did not. The decisive factor here seems to include the *distribution* of the cubically aligned grains: if the cubically aligned grains form a continuous matrix, as for instance is illustrated in Fig. 8a, the curves will be of the type under discussion. A continuous matrix is usually formed in the range of 60 to 70 per cent cubically aligned grains.

These characteristic tensile-strength and elongation curves are related to another phenomenon evidenced by copper strip containing high percentages of cubically aligned grains. This phenomenon is the distinctive type of rupture that is encountered in an Erichsen cup test. This fracture is shown in Fig. 24, where the breaks in the Erichsen cup may be seen occurring at 0° and 90° to the direction of rolling. This behavior of copper was first noted by v. Göler and Sachs.¹⁵ In Fig. 25, the tensile strength, the elongation, and, derived from these two values, the true tensile strength* for a specimen that yields four such tears in an Erichsen cup are plotted. Since the stresses developed in the copper strip during the drawing of the cup are radial tensile stresses and approximately equal, they may be represented as a circle, as in Fig. 25d. As the drawing of the cup proceeds the radial stresses increase until the limit set by the true tensile strength is reached when the metal fails. Since the true tensile strength is a minimum at 0° and 90° to the direction of rolling, the failure occurs first at these points.

This peculiarity offers a means of quickly testing for the amount of cubically

* True stress (Ludwig's true stress) is the actual stress in the test piece, corrected for the change of area during the test. It is equal to $S_0(1 + \epsilon)$ where ϵ is the unit elongation and S_0 is the stress computed on the original area.

aligned grains present in a structure. Cups with definite rectilinear tears in the direction of rolling and counter to it indicate a cubically aligned structure from 60 to 70 per cent up to 100 per cent; rectilinear tears with rounded corners indicate a cubic structure from 30 or 40 per cent to 60 or 70 per cent; round or circular breaks, from 0 to 30 to 40 per cent. Only a moderate amount of experience is needed to make these rough subdivisions.

The tensile properties of copper strip containing less than 60 to 70 per cent cubically aligned grains assume entirely different patterns from those just discussed. In Fig. 26 the directional properties of copper strip with low percentages of cubically aligned grains are reproduced. The fact that these curves are not equal at all angles to the rolling direction even where there are no cubically aligned grains present shows that there is some form of preferred orientation present—perhaps of too low a symmetry to be positively identified by photomicroscopic means, yet definite enough to make the distribution of properties uneven.

The tensile properties of soft copper strip that has been previously rolled from totally cubically aligned material are given in Fig. 27.

The development of ears in cups drawn from soft copper sheet is related to the degree of orientation found in copper strip. In Fig. 28, the percentage ear height is plotted as a function of the percentage of cubically aligned grains. It is noteworthy that strip containing less than 60 to 70 per cent cubically aligned grains still can produce ears at 0° and 90° to the direction of rolling. This relationship is more direct than any relation between ear height and final annealing temperature, for instance, or ear height and ready to finish annealing temperature, or ear height and final reduction by cold-rolling, since these factors in various combinations can produce a widely

varying percentage of cubically aligned grains in the final strip.

It should be pointed out here, of course, that each drawing operation is a separate

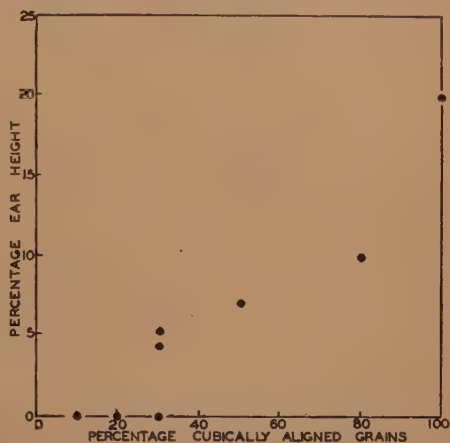


FIG. 28.—VARIATION OF EAR HEIGHT OF CUPS DRAWN FROM ANNEALED COPPER STRIP VERSUS PERCENTAGE OF CUBICALLY ALIGNED GRAINS. 0.040-MM. GRAIN SIZE.

problem and should be individually correlated to the microstructure of copper strip.

Cups drawn from copper strip that has been rolled from a totally cubically aligned structure and then annealed yield four ears at 45° to the rolling direction. These ears are not the same as those drawn by K. Kaiser,¹⁶ which were caused by rolling from a $[100] (120)$ structure (cf. Dahl and Pawlek¹⁷).

SUMMARY

1. The pole figures for copper rolled 53 and 91 per cent from a totally cubically aligned structure have been developed.
2. The rotation of the copper crystals when rolled from a cubically aligned position is described.
3. The variation of cubically aligned grains in soft copper strip with the severity of the final reduction for different starting conditions is reported.
4. The microstructure of soft copper sheet that has been previously rolled from

a totally cubically aligned structure is described.

5. A correlation between the rolled structures of copper when rolled from totally

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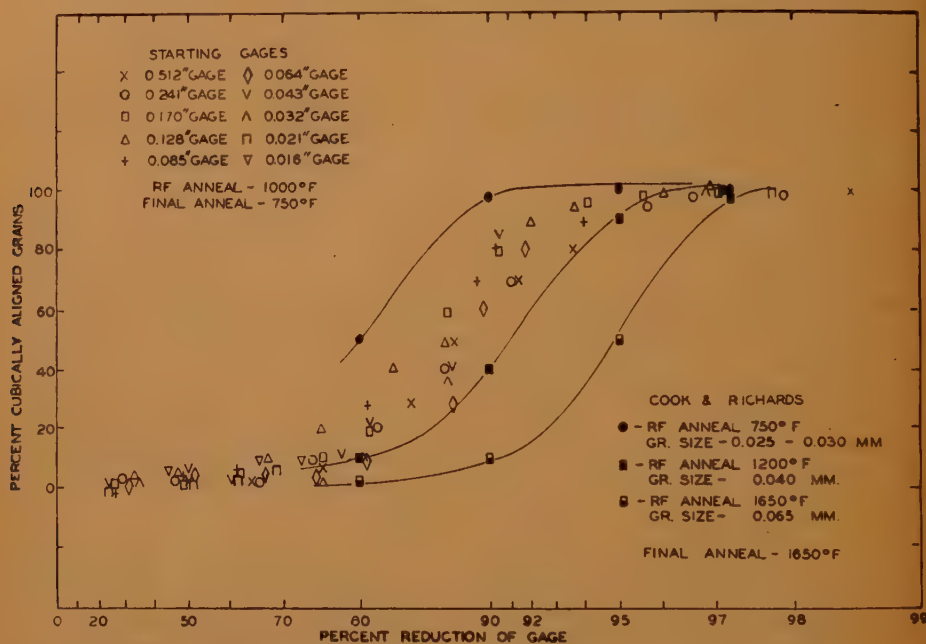


FIG. 29.—ESTIMATES OF PERCENTAGES OF CUBICALLY ALIGNED GRAINS.

cubically aligned strip and their corresponding annealed structures is drawn.

6. The tensile strength and elongation of copper for different microstructures have been determined.

7. The use of the Erichsen cup as a quick test for determining the amount of cubically aligned grains in the copper microstructure is developed.

8. A correlation between the earing tendency of copper and cubically aligned grains has been demonstrated.

ACKNOWLEDGMENT

The author wishes to express his gratitude to Mr. H. P. Croft, Assistant Director of Research, Chase Brass and Copper Co., Cleveland Mill, for his advice and suggestions, which have been so helpful in the course of this work.

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ADDENDUM

Since this paper was written, an article by Cook and Richards has been published in the *Journal of the Institute of Metals* (July 1941), which contains some points of interest, relevant to the present paper.

1. In their article, Cook and Richards have presented, among others, 12 photo-

micrographs of copper strip cold-rolled various degrees from a randomly oriented structure and then annealed at a constant temperature, the ready to finish anneal having been varied. Notwithstanding the dangers of assessing the percentage of cubically aligned grains from photographs of such small microstructural areas, the author has made such estimations and plotted them as shown in Fig. 29. A comparison between Cook and Richards' results and those reported in this paper may readily be seen.

2. In the case of copper strip cold-rolled

from totally cubically aligned structure obtained during an anneal of 1200°F. and 1650°F., Cook and Richards, on the basis of X-ray data, state: "even in strips with rolling reductions of 90 to 95 per cent only closely aligned double-texture, i.e., $(110)\bar{1}\bar{1}2$ and $(110)\bar{1}\bar{1}2$, crystals are present." This corresponds with the strip shown in Fig. 17.

3. For material rolled and annealed, they find that a reduction of 25 per cent is necessary to remove any preferred orientation that was present before the rolling. This substantiates the minimum found in the curves in Fig. 13.

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